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Papers Presented

at

Third Ontario

INDUSTRIAL

WASTE

Conference

JUNE 10th, 11th, 12th, 13th,
1956

SPONSORED BY
THE POLLUTION CONTROL BOARD
OF ONTARIO

AT THE
Delawana Inn
Honey Harbour, Ontario.

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THIRD ONTARIO INDUSTRIAL WASTE CONFERENCE

This brochure contains the papers presented at the Third Ontario Industrial Waste Conference held at Delawana Inn, Honey Harbour, Ontario, on June the 10th, 11th, 12th and 13th, 1956. The Conference was sponsored by the Pollution Control Board of Ontario, the purpose being to focus attention on industrial wastes and to determine means for treatment of these wastes. The papers are printed in the order in which they appeared on the program.

These Industrial Waste Conferences, the first of which was held in 1954, are intended to deal with one aspect of the pollution problem. Industrial growth in Ontario has been proceeding rapidly in recent years. This involves wastes of many kinds and of a complex nature. Some of these are very difficult to treat, and, since they are changing continuously with the changes in industrial processing, it is important that measures be available to control these wastes and thereby to prevent pollution of streams and other watercourses. The hope of these Conferences is that there will be clarification of the methods best designed to treat the wastes and that there will be an exchange of information among industry, municipalities and all engaged in these activities. Publication of the papers given at the Conference is done for the purpose of making the information available to as large a number of persons as possible. This information can be used freely by anyone who wishes to make use of it.

The Pollution Control Board is concerned with both industrial pollution and domestic sewage. Both are significant items in the pollution of watercourses, and it is equally important that each be dealt with in an efficient manner if pollution of streams is to be kept in check. Sewage treatment varies to a lesser degree than does industrial waste. No particular emphasis is given in this Conference to methods for dealing with sewage.

The Pollution Control Board consists of members from those Departments of the Provincial Government interested in or having obligations in respect to pollution control. Joint action by members of the Board makes it possible to co-ordinate efforts for pollution abatement. Some Departments are concerned with certain aspects of pollution while others are involved in other effects on stream. It is necessary that these be co-ordinated if the watercourses of the Province are to be maintained in a condition that they may serve best the purposes for which they were intended.

The Pollution Control Board is grateful to all those who have contributed papers to the Third Industrial Waste Conference and to those who have assisted in any way in making this Conference possible.

For further information write to The Pollution Control Board, later called "Water and Pollution Advisory Committee" of the Ontario Water Resources Commission, Parliament Buildings, Toronto.

D.S. Caverly, Secretary.

A.E. Berry, Chairman.

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ETHYL ALCOHOL FROM SULFITE WASTE LIQUOR
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Although the production of ethyl alcohol by fermentation of the sugars present in the sulfite waste liquor from wood pulp mills is not a new process, there are only three sulfite or cellulose alcohol plants operating in North America. One is located in the United States and two in Canada. However, considerable quantities of alcohol have been produced during the past 50 years in plants located in Europe. This paper will describe in some detail one of the largest and most modern of the cellulose alcohol plants.

The plant is owned and operated by Commercial Alcohols Limited, an affiliate of the Canadian International Paper Company, and is located adjacent to C.I.P.'s large pulp and newsprint mill at Gatineau, Quebec. All of the paper mill's recoverable sulfite waste liquor, totalling 5 to 6 million gallons per week, is utilized by the alcohol plant. Steam, water and electric power are also obtained from the paper mill.

The process can be divided conveniently into three basic operations:-

- (1) Preparation of the sulfite waste liquor for fermentation.
- (2) Fermentation of the sulfite waste liquor.
- (3) Recovery and purification of the alcohol produced.

OPERATION I - Preparation of the Sulfite Waste Liquor
for Fermentation.

The sulfite waste liquor as received from the paper mill contains about 10% solids, of which 15 to 20% are reducing sugars that are formed by hydrolysis of the hemicelluloses in the pulp wood during the digester cooking operation. Approximately 70% of these sugars are fermentable or hexose sugars, principally mannose and glucose.

The liquor from the paper mill is received hot at about 150°F. and enters the first of seven wooden storage tanks connected in series. The liquor flows by gravity through each of the tanks and is finally pumped from the last tank into the alcohol plant. The seven tanks, having a total capacity of 900,000 gallons, or about one day's production of sulfite waste liquor, provide sufficient liquor storage to operate the distillery continuously even though the paper mill is shut down for one day each week. The liquor remains hot, and therefore sterile, during its passage through the storage tanks, thus minimizing the possibility of contamination of the fermentation system by wild yeasts, moulds or bacteria.

Preparation of the sulfite waste liquor for fermentation consists essentially of cooling and neutralizing the liquor to the proper conditions for optimum fermentation efficiency.

The liquor, which is pumped continuously from the final storage tank, is cooled with water in a bank of 36 tube-in-shell heat exchangers. The final liquor temperature is controlled automatically to about 88° F., the optimum level for fermentation. The resulting hot water leaving the heat exchangers is used as boiler feed water by the paper mill. The heat exchangers transfer about 20 to 25 million btu/hr and can handle up to 40,000 gph of sulfite waste liquor.

The sulfite waste liquor flows from the coolers through a 3,000-gallon reaction vessel where the pH is raised from 2.5 to about 4.7 by the continuous addition of a 15% lime slurry. The reactor is divided by means of baffles into three compartments, each provided with a turbine type agitator. The liquor and the lime slurry are fed in at the top of the vessel, are intimately mixed, and flow out through the bottom. The flow of the lime slurry is regulated automatically by a continuously controlling and recording pH meter. With this system, the pH in the fermenters is controlled to within plus or minus 0.05 of a unit.

The lime slurry is prepared and stored in two 6,000-gallon tanks, one tank being used while the other is recharged. Pulverized hydrated lime (325 mesh) is stored in a 120-ton capacity hopper, and is conveyed to the tanks through a rotary bin valve and screw conveyor. Recharging of a tank is accomplished automatically from a central control panel. The tanks are instrumented completely so that once the charging system is actuated the correct amounts of water and lime are added in the proper sequence and the system then shuts off.

The hydrated lime is received in railway box cars and is transferred to the storage hopper by a pneumatic conveying system. A freight car holding 30-35 tons of lime can be emptied by this system in about six hours by one man. Approximately 20 pounds of hydrated lime are required for every 1000 gallons of sulfite waste liquor processed.

OPERATION II - Fermentation of the Sulfite Waste Liquor

The cooled and neutralized liquor leaving the reactor flows through 40-mesh screens, which remove any coarse solids such as pulp or particles of unreacted lime, and then into the first of seven fermenters.

Fermentation is carried on continuously under anaerobic conditions in seven 100,000 gallon closed wooden fermenter tanks connected in series. The fermenting liquor flows by gravity through the fermenters, each of which is equipped with a 25-horsepower propeller-type agitator to provide a rapid and efficient fermentation.

A 10% slurry of yeast is fed continuously to the first fermenter. The yeast, a strain of *Saccharomyces cerevisiae* that has been acclimated to a sulfite waste liquor environment, is obtained by centrifuging part of the completely fermented liquor or beer leaving the final fermenter. The balance of the fermented liquor, along with the partially

clarified beer from the yeast separators, flows to a 100,000 gallon wooden beer well. The hold-up time in the fermenters, or the effective fermentation time, varies from 16 to 21 hours, depending on the processing rate. Fermentation is essentially 100% complete at the end of the cycle, with about 80 - 85% of the fermentation taking place in the first two fermenters. A small amount of a 20% aqueous ammonia solution is fed continuously to the first fermenter to supply sufficient nitrogen to maintain an adequate and healthy yeast population. By-product carbon dioxide gas is recovered from the first two fermenters and is used as a prime raw material in an adjacent plant where 85% Magnesia Insulation is manufactured.

The beer, which contains about 0.8% alcohol by volume, is pumped from the beer well to the distillation unit.

OPERATION III - Recovery and Purification of the Alcohol Produced

The alcohol is stripped from the beer, purified and rectified in a five column distillation unit capable of processing up to 40,000 gph of beer and producing 450 gph of alcohol, of which over 85% is high purity cologne spirits. Because of the relatively low concentration of alcohol in the beer (molasses and grain beers average 6 - 9%), steam consumption and heat economy are important economic factors in the distillation operation. Consequently, the unit has been designed to obtain as high a thermal efficiency as possible. In addition, features have been incorporated in the distillation unit to make possible the production of high quality cologne spirits.

The five columns in the unit are (1) an atmospheric beer still or stripping column, (2) a purifying column, (3) a vacuum rectifying column, (4) a vacuum "heads" column, and (5) a vacuum "tails" column.

The beer still is 126 inches in diameter, 55 feet high and operates at atmospheric pressure. Beer from the beer well is fed continuously to the beer still, after being pre-heated in heat exchangers with the hot stillage discharged from the base of the column. Direct low-pressure steam enters the bottom of the column and the stripped alcoholic vapors and other volatile materials are drawn from the top. Stillage, containing the non-volatile portion of the beer (lignosulfonates, non-fermentable sugars, and some dead yeast) is pumped continuously from the base, through the beer pre-heaters, and is discharged.

The heat contained in the vapors leaving the top of the column is sufficient to operate the rectifying column and the heads and tails columns, with the only additional steam required being that used in the ejectors which maintain vacuums on the three columns. A part of the vapors is condensed in the calandrias of the heads and tails columns; the remainder is condensed in a vacuum steam generator which provides sufficient steam (at about 15 inches Hg vacuum) to operate the rectifying column. The condensate, or high wine, from the two calandrias and the vacuum steam generator is collected in a 2,000-gallon drum from which it is fed to the purifying column. The high wine contains about 12 to 14% alcohol.

The purifying still is a 43-inch diameter hydroselction column

60 feet high. The feed, preheated by the base discharge in tube-in-shell heat exchangers, enters at mid-column and direct steam is fed to the base. The feed rate is controlled automatically by the level in the beer still condensate drum. The heads, consisting mainly of volatile aldehydes, higher alcohols, "wood oils", volatile sulfur compounds, sulfur dioxide and some alcohol, are condensed in a steam generator which produces a small portion of the steam that is used in the beer still. The non-condensibles, chiefly sulfur dioxide, are vented to the atmosphere. Part of the condensate is returned to the top plate of the column as reflux; the remainder is removed as a "heads" fraction. The base discharge, containing approximately 12% alcohol, provides the feed for the rectifying column.

The purifying column functions both as an extractive distillation column, with water as the extracting agent, and as a reaction vessel. Hot dilution water is fed to the top plate of the column along with the reflux to effect the extractive distillation of the alcohol-soluble impurities. The high temperature and pressure in the column cause certain chemical reactions to take place which convert impurities, normally difficult to separate by ordinary distillation, to non-volatile polymerized substances that remain in the base discharge. These substances are eliminated in the subsequent rectification. The base draw from the purifying column, after passing through the purifying column feed preheaters, is cooled with water to the feed plate temperature of the vacuum rectifying column in a tube-in-shell heat exchanger. The cooled high wine is fed into the 102-inch diameter still at mid-column at a rate that is controlled by the base level in the purifying column. The column operates at a pressure of 260 mm Hg and is heated by direct steam generated in the vacuum steam generator used to condense the beer still vapors. All the non-volatile material in the high wine feed is contained in the stillage that is pumped from the base of the column.

The product is withdrawn from the upper part of the column at a strength of approximately 97% alcohol by volume. The rate of draw-off is controlled automatically by the preset mid-column temperature.

The overhead vapors, which contain a high concentration of volatile impurities, are condensed in a tube-in-shell condenser. Part of this condensed heads draw is returned to the top plate as reflux; the remainder is returned to the beer still condensate drum.

The higher alcohols or fusel oil, along with some "wood oils", accumulate on the mid-column plates and are drawn off as a side cut. This fusel oil draw is pumped continuously to a decanter where the alcohol-soluble but water-immiscible oils are separated from the ethanol in the draw by dilution with water. The fusel oil, which is lighter than water, and the wood oils, which are heavier than water, separate out as top and bottom layers respectively and are drawn off. The dilute alcohol middle layer is returned to the beer still condensate drum.

The product from the rectifying column, while being a high strength alcohol suitable for most denatured grades, still contains some impurities, the chief one being methanol. This methanol originates in the digesters at the paper mill, having been formed during the cooking process from the methoxyl groups in both the lignin and hemicelluloses

in the pulp wood, and is present, therefore, in the sulfite waste liquor produced. The methanol, along with small amounts of volatile impurities, is removed from the ethanol in the heads column. The 58-inch diameter heads column and the 54-inch diameter tails column are each 50 feet high and operate at about 200 mm Hg vacuum. They both are heated indirectly by condensing some of the beer still vapors in a calandria in the base of each column.

The product from the rectifying column is fed into the upper part of the heads column. The methanol in the feed, having a lower boiling point than ethanol, is concentrated in the overhead vapors along with the remaining volatile impurities such as aldehydes, and is removed in the heads draw as an anhydrous methanol-ethanol mixture. This draw is controlled automatically by the preset temperature at the top of the column. Part of the heads draw is returned to the top plate as reflux while the remainder is stored for use as a denaturant or for sale as a solvent.

The base discharge from the heads column is at about the same alcohol strength as the feed to the column but now contains no methanol. The heads column product is fed to the tails column for the final purification step, the rate of feed being controlled automatically by the base level in the heads column.

The feed enters the final still below mid-column and the cologne spirits product is withdrawn under automatic control. Any last traces of volatile impurities that might be present in the feed to the column are concentrated in the overhead vapors which are condensed in a tube-in-shell condenser. Part of the condensate is returned to the top plate as reflux and the remainder is sent to the beer still condensate drum for recycling. Any remaining higher boiling impurities, such as higher alcohols and certain esters, are concentrated in the base and are removed as a tails draw and stored for use as a denatured grade product. The draw rate is controlled automatically by the base level.

The methanol draw, the alcohol draw for denatured grade product, and the cologne spirits draw are collected in separate closed receivers in accordance with the Government Excise regulations. From the receivers, the various products, after having been approved for quality by the control laboratory, are weighed and tested in the presence of Government Excise Officers and then pumped to storage.

Process and Quality Control

In order to maintain continuous production of a high quality ethyl alcohol, the distillery is instrumented as completely and thoroughly as is practical. Nearly all the instruments are operated pneumatically and are located at three control stations: one station in the sulfite waste liquor cooling and neutralizing area, another in the fermentation area and a third in the distillation area. By means of these instruments the entire distillery is started up, operated and shut down by only three operators per shift.

While the continuous operation and extensive instrumentation insures relatively uniform product quality, the intermittent batch

operation of the digesters at the mill tends toward variations in the sulfite waste liquor composition from cook to cook. In addition, changes are made in the grade of pulp produced, the type of wood used, and the cooking conditions. These variables affect the percent of solids, sugars, free and combined sulfur dioxide, methanol, and calcium sulfate present in the liquor.

To minimize the effect of these variations, the quality control laboratory carries out routine chemical and physical analyses on the various process streams in the alcohol plant. The results of these analyses are used to determine the optimum operating conditions for the liquor being processed. Yeast cell count and viability tests are performed regularly to insure maximum fermentation efficiency. Routine bacteriological tests are also carried out on the liquor at various stages in the process to guard against bacterial contamination of the fermentation system.

In addition to these analyses each receiver of the final ethyl alcohol product is tested for product quality before being put into storage. An alcohol receiver that does not meet the Company specifications for cologne spirits, which are more rigid than both the U.S. and British Pharmacopoeia specifications, is put into storage for denatured grade alcohol.

Depending on the sugar content of the sulfite waste liquor, a total of 2.5 to 3 million gallons of alcohol can be produced annually, of which about 85% is high quality cologne spirits.

Production of 85% Magnesia Insulation

About 2.5 - 3 million board feet of 85% Magnesia Insulation are produced annually for Canadian Johns-Manville in an adjacent plant. This plant utilizes some of the 150 - 190 million cubic feet of by-product carbon dioxide produced annually by the distillery. It is interesting to note that about 30% of the weight of the final product is provided by this carbon dioxide.

In this process the fermenter gases from the first two fermenters, where about 80 - 85% of the fermentation takes place, are pumped directly to a 3,500-gallon continuous carbonator in the magnesia plant. The carbonator is charged continuously with water, a solution of magnesium bicarbonate, and finely pulverized magnesium hydroxide. The bicarbonate and hydroxide react to form magnesium normal carbonate crystals, and the fermenter gases, containing about 95% carbon dioxide, are dispersed in the carbonator by a high speed agitator to maintain the required bicarbonate concentration. The dilute suspension of magnesium normal carbonate crystals overflows continuously to an Oliver vacuum filter where the crystals are concentrated and put into storage as a 20% slurry. The filtrate, which contains magnesium bicarbonate, is returned to the carbonator. To control the carbonation rate, a constant bicarbonate concentration is maintained in the carbonator by adjusting the feed rates of the hydroxide and make-up water.

To make the molding slurry, the 20% suspension of magnesium normal carbonate crystals is blended with asbestos fibre in 400-gallon

batches. The asbestos is added as a temperature-resistant binder to give added strength to the final product.

Just prior to molding, the carbonate-fibre slurry is diluted with hot water which partially converts the magnesium normal carbonate crystals to magnesium basic carbonate. This reaction takes from eight to ten minutes, after which the slurry is molded into insulation.

Two molders of the reciprocating filter press type, designed by Johns-Manville, and capable of molding three-foot lengths of pipe covering or block insulation of various sizes and thicknesses, are required for present production. A metered charge of dilute magnesium basic carbonate and asbestos fibre is dumped into the mold box which rests on one of two reciprocating pallets covered by wire mesh. A ram, to which is attached a perforated steel molding head also covered with wire mesh, descends into the mold box and the excess water is pressed out of the slurry. The plastic-like residue of magnesium basic carbonate and asbestos fibre takes the shape of the space between the pallet, the molding head and the mold box sides.

After a piece has been molded, the ram and the mold box rise, the pallet with the freshly molded piece swings from under the mold box and the empty pallet moves into position. Then the piece is removed from the pallet, placed on a curing table, and later placed in a drying car. While this is taking place the mold box descends, a fresh charge is metered into the box, and the molding cycle is repeated.

The molders are hydraulically operated, and the molding sequence is controlled automatically by a series of electrically driven adjustable cams that open and close the various valves in the hydraulic system, either directly or by triggering solenoid valves. Each molder is operated independently through its individual control system.

The molded insulation is dried for about 24 hours in forced-air tunnel-driers at about 300-340°F. The dried blocks are removed from the drier cars, inspected and packed in cartons for shipment. The dried pipe covering, made in half sections, must be trimmed so that the two pieces are inspected, made into whole sections by wrapping with cotton cloth, and packed in cartons for shipment.

SULPHITE LIQUOR PRODUCTS

J. K. Russell

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The various processes for the production of what are termed chemical pulps are in essence treatments which free the fibrous cellulose from the lignin or cementing material which holds the fibres together. There are a number of these processes, the most important economically being the sulphate or kraft process and the sulphite process.

In the sulphite process the wood in form of chips is treated with an aqueous solution of calcium bisulphite which contains a considerable amount of excess or uncombined sulphur dioxide. The treatment is carried out as a batch process at a temperature of about 140°C. and pressures of 80-90 pounds. At the completion of the treatment, generally 8 to 10 hours, the lignin, now in form of an aqueous solution is separated from the fibrous wood pulp and normally rejected to the sewer.

In its natural state lignin is a colourless or light straw coloured amorphous solid, insoluble in water or organic solvents. Its constitution is still not satisfactorily established in spite of extensive investigation but there is now substantial agreement that the fundamental unit is a benzene nucleus with an aliphatic, probably a propyl side chain with several hydroxyl and methoxyl units distributed between the side chain and nucleus. During the digestion of the wood one or at most two sulphonic groups are added probably on the side chain, giving rise to a material which is generally referred to as lignosulphonic acid. Lignosulphonic acid cannot, however, be considered a single compound. As normally obtained both the degree of sulphonation and the molecular weight will vary widely.

Lignin sulphonates account for about 70% of the total solids in the spent liquor. The balance is made up of sugars, monosaccharides both pentoses and hexoses and polysaccharides with smaller amounts of inorganic constituents, sulphates and sulphites of the cation, generally calcium, present in cooking liquor.

For convenience the products obtained from sulphite liquor may be divided into three categories - (1) those obtained from the sugar fraction through microbiological processes, (2) those which are dependent on the properties of the sulphite liquor modified or unmodified and (3) those obtained from the lignosulphonate fraction by chemical conversion.

Fermentation Products

The relatively high proportion of sugars in the liquor had early suggested that it might provide a suitable raw material for a fermentation process for the production of ethyl alcohol. Hexoses,

which are suitable nutrients for alcohol producing yeasts account for about 60% of the total sugar content and may, depending on conditions in the cooking process, be present in amounts up to 20 grams per liter. The process presents no serious operating problems. Neutralization with lime, with or without previous steam stripping is necessary in order to establish suitable pH conditions for yeast growth. The low concentration of alcohol in the fermented mash gives rise to high heat consumption in recovery and it is probable that this is the largest single item of operating cost.

A number of plants were established as early as the first World War and some of these are still in operation. The process has been attractive in Europe especially in Scandinavia where the use of the product as motor fuel has been favoured because of the lack of domestic sources of petroleum. Two plants are in operation in Canada and one in the United States. It is probable that further extension of the process has been hindered by competition, actual or potential, from low cost alcohol produced from by-product ethylene.

A somewhat more recent development is the utilization of the carbohydrate fraction for the growth of *Torula* yeasts. These yeasts differ from alcohol producing yeasts in that they can ingest pentoses as well as hexoses so that the total sugar content can be utilized for their nourishment. The process was established in Germany during the last war when shortages of normal protein human foodstuffs fostered the production and use of the high protein, vitamin rich yeasts. Their use as human foodstuffs has now lapsed but they do find a place in animal feedstuffs. Their chief value lies in their high vitamin content. As a source of protein they cannot compete with materials such as soya bean meal and linseed meal. Consequently it would not be expected that they would find a place in the feeding of ruminants and other stock which can produce their own vitamins. They are valuable in the feeding of poultry and where the poultry population is large enough it might be expected that they would find a profitable market. There is one plant in the United States producing *Torula* yeast and the construction of another has been announced. There are none in Canada.

Vanillin

Vanillin is the only simple product, apart from ethyl alcohol which is obtained in a state of high purity from sulphite liquor and is the only product which is produced in commercial quantities through chemical conversion of the lignin fraction. It is presumed that it is produced by splitting off of the sulphonic group with subsequent conversion of the propyl side chain to an aldehyde group. It may be produced by alkaline hydrolysis or by mild oxidation in an alkaline medium. Of the four plants now known to be in operation two are said to be producing through hydrolysis and two through oxidation.

The principal, in fact the only outlet for vanillin at the present time is in food flavouring. The market is necessarily very limited and is governed by the popularity of vanilla flavouring. The use of vanillin as an intermediate in industrial synthesis would do much to broaden the market. This has been given considerable attention and attempts have been made to produce the material at a price which

would encourage more general use. One manufacturer is now offering a less highly purified grade at a lower price.

There are two plants producing vanillin in Canada and two in the United States.

Adhesive Uses

The appearance and obvious properties of sulphite liquor have early suggested that it might have valuable adhesive qualities. A concentrated solution of 50% solids or more is tacky and on drying it forms a tough glassy film. In view of these properties it might be supposed that it would serve as a general adhesive replacing starch, dextrin, silicates and even animal glue in number of uses. These expectations have not been fulfilled. When used as a wet adhesive, it has been found that it does not have the "tack", as understood in the adhesive field, required for the fast development of a bond. Equally serious is the loss in strength in the dried bond on aging, possibly through loss of the small amount of water required for plasticizing the film.

Numerous attempts have been made to overcome these drawbacks especially in the field of remoistenable adhesives for sealing tapes and similar use, (1, 2). Insofar as is known, more of these have been successful to the point of commercial use.

More success has been attained in a number of less demanding uses. Among these mention might be made of a binder for refractory brick where it improves dry strength and facilitates handling of the brick prior to firing. A somewhat similar use is found in a binder for pelleting of zinc ore concentrates and iron ores for the prevention of stack losses in smelting. Another adhesive use is in the preparation of linoleum cements for the cementing of linoleum tile and other floor coverings. All these uses have in common the fact that a weak adhesive will give the required bond strength and that the value of the products involved does not permit more than a minimum cost for the adhesive. Consequently the producers' margins are such that a satisfactory pay-off on a necessarily expensive plant can hardly be achieved. The development of good grade adhesive from sulphite liquor either through modification or compounding is yet to be achieved.

Soil Stabilization

The soil stabilization properties of sulphite liquor are probably due to a certain extent at least to its adhesive properties although there has been some speculation as to whether its surface active action, as a deflocculant, may not also contribute to its stabilizing effect. The appearance of highways which have been treated for the prevention of dusting would lend support to the adhesive mechanism. Surfaces on treated roads become so hard that they cannot, when dry, be bladed for correction of contour and pot-holes. On the other hand, the high degree of compaction which is achieved after treatment for stabilization under an asphalt-wearing coat would indicate that disperions or deflocculation must play some part in the increases in bearing strength achieved. Similarly in the prevention of frost heave, where sulphite liquor has been found to be singularly effective, there is every

indication that surface active properties, either through a decrease in the permeability or through some alteration in the surface properties of the soil particles, are of paramount importance.

The treatment of road surfaces with sulphite liquor originated in Sweden where dirt and gravelled roads in the vicinity of the pulp mills were treated extensively with raw dilute liquor obtained directly from the mills. More recently this practice has been taken up in the mid-west United States, especially in Wisconsin. Results were reported to be good in that dust nuisance was almost entirely eliminated and the general durability of the roads improved. Some experiments were undertaken in this country, in the Province of Quebec, and the results were in agreement with Swedish and United States experience insofar as almost complete alleviation of the dust condition was achieved. Some difficulties arose, however, with regard to maintenance in that blading of the road in a dry condition was found to be virtually impossible. The result was that serious pot-holes developed, possibly made worse by the hard surface which had been produced on the road. It would seem likely that these difficulties might have been overcome through blading when the road was wet but this solution did not appeal to road maintenance crews and the experiment was discontinued.

While results in the treatment of secondary roads for the prevention of dusting have not been encouraging more success has been achieved in the stabilization of the base course under an asphalt wearing coat. Application is generally made at the rate of 0.7 to 0.8 lbs. solids per square yard of surface. It is applied as a 25 to 27% solution after the placing of the final gravel after which the road contours are corrected by blading. The bearing strength of the gravel course is noticeably improved so that if desired less gravel may be used or alternatively a thinner wearing coat may be applied. It also serves as a primer to promote the adhesion of the asphalt and eliminate a special treatment for this purpose. At the same time an acceptable surface and elimination of dusting is provided during construction and a considerable saving is achieved through decreasing the amount of correction required before application of the wearing coat. It is believed that very good results might be obtained through the application of sulphite liquor with the tempering water when mechanical consolidation of the sub grade is practiced but this has not been tried out in actual construction.

Approximately 200 miles of highway in the Province of Quebec has been stabilized with sulphite liquor and the results have been uniformly good. Credit should be given to the various members of the staff of the Quebec Department of Roads for their co-operation in the early stages of this project. Credit should also be given to Mr. Guillaume Piette of Laval University and Mr. Jacques Hurtibise of the Ecole Polytechnique of Montreal who have at various times served as consultants on the project.

A less obvious type of soil stabilization in which sulphite liquor has been found to be very effective is the prevention of frost heaving. The frost heaving of soils, as distinguished from the movement caused by freezing of the soil water, is characterized by the formation of ice lenses or layers of solid ice at various depths down to the frost line. Normally they might not be expected to give rise to a change in

surface level or more than six inches or a foot but might in certain circumstances cause level changes of two or more feet. Gravel and sand soils are not subject to heave nor are impervious clays. Maximum heaves are usually found in soils intermediate between these types such as are designated as silts or sandy silts.

The effect of sulphite liquor on frost heaves was found by Dean Hardy and his co-workers at the University of Alberta in the course of a laboratory screening of a number of materials for their effectiveness (3). His initial findings were confirmed and it was found that by the application of about 2% sulphite liquor solids, heaving on a typical heaving soil could be virtually eliminated under laboratory conditions. This effect has been confirmed in the field first by Hercy in a conveniently located curling rink and later on a railway embankment (4). Subsequently a series of tests were carried out in the Lake St. John area in co-operation with the Canadian National Railways. These are uniformly successful and have been extended each year since that time. Some failures have since occurred, satisfactory reasons for which can usually be postulated, but in general results have been good. One encouraging outcome, the more so because it was not entirely expected, has been the persistence of the effect through several seasons. There has in fact been some indication of further improvement in the second and third season following application.

A completely satisfactory mechanism for the action of sulphite liquor has still to be advanced. Frost heaving is presumed to occur through a capillary movement of water from the water table to the frost line where it freezes and, as the process continues, produces an ice lens the thickness of which depends on the time and temperature of exposure. The fact that heaving is found only in soils of an intermediate particle size would suggest that the capillarity of the soil is the determining factor. Similarly Hardy's observation that certain other surface active materials have a similar effect to sulphite liquor would suggest that the latter produces its effect through a modification of the soil capillarity. Whether this occurs through an increase in density brought about by a deflocculation of the soil particles or through a modification of the surface properties of the soil particles, following adsorption of lignosulphonates, is not known.

Dispersant Applications

One of the most important and diversified fields in which sulphite liquor, or rather lignosulphonates are finding increasing acceptance is the dispersion of aqueous slurries. Lignosulphonates are polyelectrolytes in which the sulphonic group supplies a hydrophillic group in conjunction with the hydrophobic lignin nucleus. The surface active properties conferred are not outstanding in terms of wetting action, surface tensions are not abnormally low, but have been found to be useful in the promotion of dispersion in a wide variety of aqueous slurries. The mechanism of this action is presumed to be an adsorption of the lignosulphonate molecule on the particle surface with a resulting neutralization of the mutual attraction between the particles. In general, dispersant action is highly specific; a dispersant which is effective in one type of slurry may be ineffective or even promote flocculation in another type. Lignosulphonates are effective in a wide variety of

slurries but often only after modification. The production of dispersants for specific uses has been under active investigation in a number of laboratories but the results have not been published except as they should happen to be incorporated in patent specifications. For this reason little can be said concerning the production of the various products sold for dispersant uses.

Portland Cement

Lignins have been found to be useful in three different phases of the production and use of hydraulic cements. Two of these are in the manufacture of cement - as a dispersant or thinner in the grinding of the raw feed and as a grinding aid in the final grinding of the clinker. The third is as an additive to reduce viscosity and/or water ratios in the cement mix.

The dispersing action of sulphite liquor on cement slurry was first reported by Simon in 1925 (5). There are no further literature references until 1937-38 when a number of patents were issued to Scripture (6), Mark (7) and others (8). Following the granting of these and subsequent patents the assignees undertook the exploitation of the effect and as a result the use of sulphite liquor in concrete mixes is now an accepted practice.

Sulphite liquor serves three functions in the cement mix. It reduces the water required to give the viscosity necessary for satisfactory placing of the wet concrete and as a result of the strength increase derived from the lower water ratio is said to permit a reduction in the cement ratio in the design of a mix for any given strength level. It also promotes the entrainment of air in the concrete, an effect which adds to the durability particularly in locations where the concrete is subjected to repeated freeze-thaw cycles. Its third function is that of a retarder in the set. This may sometimes be undesirable but there are occasions, as for instance, in the placing of concrete at high ambient temperatures where some retardation is essential. This property has lead to widespread use of lignins in the cementing of oil wells where extremely high temperatures may be encountered in the deeper wells.

Lignins exert a marked dispersing effect on slurries of ground limestone with shale or clay, which as raw materials in the manufacture of Portland cement, are fed to the cement kilns for sintering (9). Moisture contents of the slurries normally vary between 30 and 40% and by virtue of the reduction in viscosity they may be reduced to 22 to 30% with a dosage of about 0.25% on the dry weight of the slurry or about 1 pound per barrel of finished cement. The reduction in water content permits substantial savings in fuel in the sintering operation as well as an increase in the kiln output. The dispersant when added to the raw feed to the primary mill acts as a grinding aid and under favourable circumstances may increase the mill output by 20-30%. The power savings involved are small but the increased production may in some cases be an important consideration.

Considerable effort has gone into the investigation of this effect and a number of plant trials have been carried out both in Canada

and the United States. No widespread use has developed partly because a resistance to innovation on the part of the cement plant operators. Objective difficulties have also been encountered, chiefly in connection with the operation and control of the kiln under changed moisture conditions. It is felt however that the use of lignins in this phase of cement manufacture will eventually be established to the mutual advantage of the cement manufacturers and the lignin producers.

Lignins now find a use as grinding aids in the grinding of the clinker in the final stage in the production of cement. Here they are used in combination with an alkanolamine, generally triethanolamine, the mixture having properties as a grinding aid not possessed by either components. The grinding aid is used in very small quantities usually less than 0.1% on the clinker and increases the grinding rate by as much as 40%. It has not come into general use but has been found effective, in the grinding of high early strength cements where the finer grind required makes the use of a grinding aid attractive. Use has been very limited in Canada but has been extensive in the United States.

Gypsum Wallboard

Lignins are also effective as dispersants and retarders in the manufacture of gypsum wallboard. Here the gypsum stucco is slurried with water and spread between two sheets of paper after which it is carried through a drier for the removal of water in excess of that required for the formation of the calcium sulphate dihydrate. Any reduction in water content of the slurry obtained through a decrease in viscosity is reflected in lower fuel costs and increased drier capacity. Retarding of the set and better flow characteristics of the slurry are further advantages. All the wallboard plants in eastern Canada and a number in the eastern United States are now using lignins of some type.

Oil Well Drilling Muds

Dispersants, which are known as thinners in this field, play an important part in the formulation of oil well drilling fluids. The fluids are essentially suspensions of a swelling clay, sodium bentonite, in water and they perform several functions the most important of which are the transport of cuttings to the surface and the sealing of the hole against gas pressures which may develop. Viscosity characteristics are very important both as regards pressure drop in the mud circulation system and as regards the ability of the mud to support cuttings in their travel to the surface.

The generally accepted dispersant in drilling muds has been quebracho and in the treatment of sodium muds it is still one of the more effective thinners. Several competitive materials have been developed some of which are more effective under special conditions. There is as far as is known only one lignin based product which is competitive with quebracho in sodium based muds.

Lignins find more general use in lime based muds. These are produced by treatment of the sodium base mud, in the course of the drilling operation, with sodium hydroxide and lime to convert the sodium bentonite to calcium bentonite. They are used generally in deep wells

and particularly where anhydrite is to be encountered. Lignins are especially useful in controlling the transient high viscosities encountered in the conversion to a lime base. Several lignin products are being sold for use in this service. A number of them are used in conjunction with quebracho where some synergistic effect is found in the combination. One, at least, is effective alone.

Miscellaneous Dispersions

Lignins are used in a wide variety of dispersion applications in addition to those already mentioned. Not many of these applications are large in themselves although in aggregate considerable amounts may be required. The following may merit some mention.

Carbon Black - Carbon black slurries are used in compounding rubber by the "master batch" process in which the slurry is added to synthetic rubber latex and the whole precipitated through acidification. A dispersant is required in order to obtain a manageable carbon black slurry at the required solids. At least one lignin product on the market is satisfactory in this application.

Agricultural Insecticide - Dispersants and wetting agents are required for agricultural sulphur, DDT and other insecticides. A number of lignin products are giving satisfactory performance.

Pigments and Dyestuffs - Lignins make satisfactory dispersants and wetting agents for a number of pigments and dyestuffs. A limited amount is sold for use in applications where dispersion is required.

Leather Tanning

It might be interesting to recall that the sulphite pulp process arose out of an attempt by Mitscherlich in 1878 to prepare a tanning extract by treatment of oak wood with calcium bisulphite solutions (10). The attempt was unsuccessful but a useful paper making fibre was obtained. Since that time there have been numerous attempts to apply sulphite liquor to the production of leather from hides. Early attempts were not successful and "spruce", as it came to be known in the tanning trade, acquired a bad reputation with the tanners. This arose largely through a failure to recognize the limitations of the material.

Sulphite liquor is not a tanning material in the sense that it will impart the same properties to leather as quebracho, chestnut and the other vegetable tannins. Shrinkage temperature is improved very little over the raw hide and practically no improvement is found in the resistance to enzyme degradation. Lignosulphonates are, however, irreversibly combined with the collagen fibre and are finding a useful place in the tannery process, as a pretan in vegetable and chrome tanning and as a retan in chrome tanning. It is also finding widespread use as a filler in the finishing of vegetable tanned sole leather.

As a pretan in vegetable tanning lignosulphonates improve the penetration of the vegetable extracts and protect the hide substance from surface attack by strong tannin solutions. In retanning of chrome tanned leathers they impart certain temper properties which are diffi-

cult to obtain
time provide a lower cost replacement for the

Calcium salts are used only to a limited extent in tanning largely because of the insoluble calcium compounds formed with quebracho and other vegetable tannins and because of the calcium precipitates formed with certain of the fat liquor components. Magnesium salts have been widely used and ammonium and sodium salts are now becoming popular.

Conclusion

A reasonable question for this group to ask is when it might be expected that profitable outlets will be available for all the sulphite lignin produced in this country. That is a question to which no optimistic answer can be given. Canadian production of sulphite pulp is upwards 3,000,000 tons per year which as a rough estimate will produce an equal amount of sulphite liquor solids. Present production of lignin products, some proportion of which is exported, will certainly amount to less than 20,000 tons. The ethanol production will probably account for the partial utilization of about 150,000 tons of sulphite liquor solids. It is hardly conceivable that, under the most favourable conditions, the applications outlined here could amount to more than 200,000 tons with the partial utilization of a somewhat smaller amount for the production of ethanol.

There are not, in the present state of our knowledge, market outlets for even a substantial proportion of the available lignin. A solution will be found only in extensive systematic investigation of the properties and behaviour, especially under degradative conditions, of sulphite lignin. The financing of such a research effort is an act of faith but one which the potential rewards could well justify.

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SPRAY IRRIGATION FOR DISPOSAL OF MILK WASTES

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The disposal of dairy plant wastes by means of spray irrigation is dependent upon the practice of rigid control of waste waters within the plant. The first essential in installing a spray irrigation waste disposal system is the separation of all clear cooling waters and storm water from the floor water and washing waste. It is also desirable to eliminate sanitary sewage from the dairy waste. The second essential to the proper operation of a spray irrigation system is the rigid control of the amount of wash water used.

In the case of new plants, it is desirable to lay out the sewer system in three parts so that complete separation is made between storm and cooling water, sanitary sewage, and process wastes. The storm and cooling water which is uncontaminated can be discharged into the nearest water course or storm sewer. The sanitary sewage should be discharged to a septic tank or sanitary sewer, and the process waste discharged to the spray irrigation system.

The control of water usage within the plant is best done by providing equipment which prevents the wasting of water. Extensive use should be made of automatic shut-off nozzles on wash-up hoses. These nozzles will close automatically when they are released by the operator. A very desirable procedure is to install a tempered water distribution system in which warm water of the proper temperature for washing equipment is distributed throughout the plant. Hanging hoses are connected to this overhead distribution system and the hoses are installed alongside equipment with the nozzle hanging just above the floor. In this way the volume of water can be reduced to a minimum and at the same time the washing operation is made much more thorough through the ready availability of wash-up hoses. Both the Strahman and Lonn automatic shut-off nozzles have been used successfully.

The waste process waters are conducted to a sump at a convenient location where a pump may be installed to pump the waste to the spray irrigation field. It is desirable to provide settling and fine screening for the waste prior to its entering the pump sump. In several installations, this has been done by passing the waste through a small settling tank and by hanging a screened basket below the sewer inlet to the sump. Normally where floor drains with baskets are installed in the plant, the amount of waste collected in the screens is a minimum. Because of the water conservation practices, the volume of waste water is rather small. Some installations handling as much as 200,000 pounds of milk per day have a waste volume of only about 3,000 gallons.

In any spray irrigation system, it is desirable to spray at as high a pressure as possible since under these conditions better distribution of the waste is obtained. The pumping equipment should be capable of spraying the required volume of water at a pressure of at least

120' at the pump discharge. The nozzles in general use require a pressure of approximately 50 pounds per square inch at the nozzle. Allowances must be made for difference in elevation and pipe friction.

The pump should be of the open impeller type and normally operates at 3600 rpm in order to produce the desired pressure. There are two means of installing the pumps. In smaller installations, the pump has been installed above the pit which, of course, results in a suction lift of the waste to the pump. This is not desirable since it results in possible loss of prime which results in the failure of the pump. Installations using self-priming pumps have been made with good success. On larger installations, the most desirable procedure is to install the pumps in a dry pit taking suction through the pit wall from the adjacent wet pit. In this way, the pumps are provided with a positive suction head resulting in much more reliable operation. The cost of installing pumps in this manner is, of course, more expensive. To date, successful installations have been made using Ingersoll-Rand, Deming, and Gorman-Rupp pumps. A stand-by pump is desirable. However, there are installations operating with only one pump.

The distribution piping from the pump to the spray nozzles can be installed above the ground where only summer operation is anticipated or below ground where year-round operation is desired. The depth to which the pipe should be buried depends, of course, upon the local frost conditions. It is desirable, in any case, to so install the pipes that drainage will be obtained either to the pump pit or to drain valves installed in low points in the piping. The drain valves used on water hydrants have been used successfully for draining the underground laterals and mains of the spray irrigation system.

Spray nozzles capable of covering an area of 75' to 150' in diameter have been used. This choice is dictated by the necessity of having the nozzle openings not less than $\frac{1}{4}$ " in diameter so as to reduce the possibility of plugging the nozzles. The choice of these larger nozzles also influences the choice of the pump and pressure at which it must operate. Our experience with Rainbird sprinkler nozzles, model #80S, has been very satisfactory.

The first recent record of waste disposal by means of spray irrigation was at Donaldson, Tennessee at the Swiss Farms Dairy in 1949. This installation disposed of 12,600 gallons of waste through a 2" line with a 5 HP centrifugal pump to two sprays which were moved daily and covered two acres in ten days. This is a dosage rate of 6,300 gallons per acre per day. The average concentration of the waste was 70 pounds of B.O.D. per day.

The next installation of record was at a dairy near Camden, New Jersey installed in 1951 and designed for 75,000 gallons per day and spraying on 45 acres or a dosage rate of 1,670 gallons per acre per day. A pump sump capable of holding five to six days' waste was apparently too large and resulted in a bad odor and a rather unfavorable impression of the operation.

In 1952 an installation was made at Pickerington Creamery, Incorporated at Pickerington, Ohio. Originally this was a lagoon which

created bad odors. The spraying of the waste from the lagoon was not satisfactory because of the odor nuisance and in 1953 the installation was changed to spray fresh waste directly to the field. This installation was much more satisfactory. The waste was discharged through a 4" line buried 3' underground to a pasture where nine 2" spray nozzles were located. One spray was used at a time and the sprays were changed daily. Drain tiles under the pasture were plugged in order to eliminate the percolation of strong wastes to the stream. Cows were pastured in the field while the spray operation was in progress. There was an excellent growth of grass in the pasture. In extremely cold weather the lagoon was used rather than the sprays.

An installation was made at Schumaker's Dairies, Incorporated at Bridgeton, New Jersey in 1950. Plant wastes were discharged by gravity to an open sump pit where a 300 gallon per minute centrifugal pump was installed. Overground aluminum pipes were used for headers and laterals with spray nozzles at each 40' joint. One lateral was moved every three days. The amount of waste water sprayed daily was 75,000 gallons and it was held until the heavy processing load in the plant was over to save electrical demand charges. The irrigation pump was then started and ran only about three hours per day. The installation was originally designed for 100 acres, but used only three 10 acre fields or a dosage rate of 2,500 gallons per acre per day. The installation operates daily throughout the winter. The lines are drained at low points. Heavy ice forms on ground and fences, but causes no trouble. The milk plant bottles about 35,000 pounds of milk daily and makes about 1,000 pounds of cottage cheese a week. Caustic is drained from the bottle washer every three months to floor drains and the dilution in the day's waste volume has prevented any ill effects on vegetation.

The first Kraft Foods Company installation was made at Berwick Ontario in 1952. This installation sprayed about 3,000 gallons of waste per day through two spray nozzles. The nozzles were moved weekly and the total area covered involved about three acres or 2,700 gallons per acre per day. Plastic pipe laid above ground was used for part of the installation and galvanized wrought steel pipe for the remainder. The spray nozzles were placed on risers about 6' above the ground surface and the spray circle was approximately 100' in diameter. The installation was operated during the spring, summer, and fall only and was closed down during the winter when the waste was discharged through a large septic tank. This installation was successful in preventing complaints of odors and stream pollution during periods of low stream flow in the summer months.

A spray irrigation installation was made at Alexandria, Tennessee in 1953. The installation consisted of six spray nozzles located in a field approximately $3\frac{1}{2}$ acres in area. Wastes were drained by gravity from the plant to a sump pit and pumped through a header to laterals in the field. The header was galvanized pipe installed approximately 18" underground. The laterals were polyethelene plastic pipe laid above ground. This installation has been very successful in disposing of plant floor washing and whey. The top soil, which was very thin at the start of the operation, has developed into a heavy-rich top soil with a very luxuriant root structure from the grasses grown on the field.

In 1953 a spray irrigation installation was made at Shirley, Indiana. This system was designed for year-round operation by burying all of the headers and laterals approximately 30" deep. Galvanized wrought steel pipe was used throughout. The area available was approximately ten acres of which about six acres were provided with underground piping for spray nozzles. The spray nozzles were selected to cover an area 100' in diameter and the nozzles were spaced approximately 90' apart. Two spray nozzles were used at a time to provide for a discharge of approximately 100 gallons per minute. In addition to the underground system for plant floor wastes, an over ground system covering approximately two acres was installed for the disposal of whey on an experimental basis. Approximately 5,000 pounds of whey were sprayed on this area daily. It was found that the whey killed off the grasses, but did develop a very prolific growth of weeds in this area.

Some difficulties were encountered with the entire system due to the presence of underground tiles in the field which were not discovered until after the installation was made. It has been necessary to plug this underground tile system to prevent too rapid percolation of the wastes into the receiving stream.

We recently made an installation in South Edmeston, New York which will operate only during the summer months. In this instance we are taking advantage of the New York State stream classification which limits the amount of dissolved oxygen depletion in the stream. In this case, we expect that operation during the summer months will be adequate to meet the state standards.

A spray irrigation system was installed at Owenton, Kentucky and has alleviated a very difficult waste disposal problem. In this instance, the receiving stream was so small that 100% purification would be necessary to meet any standards. A spray irrigation system which eliminated the discharge of any waste to the stream is probably the only method that would be suitable in this case.

At Milan, Wisconsin an installation was made above ground which operates during the summer months. Large amounts of whey have been sprayed in this particular system, and while this has not been completely satisfactory, it has been a major improvement over the condition which would have resulted had the whey been discharged directly to the creek.

There are two problems which always arise in the design of a spray irrigation system. The first concerns the area of land necessary to provide the proper treatment. There are a number of factors which influence the dosage of waste on a spray irrigation field. The three most important are the slope of the ground, the type of soil, and the type of cover crop.

The slope of the ground should preferably be less than 6% and the land should be relatively free of gullies. The most ideal condition is to have a gently sloping piece of land with the installation of the pump sump at the low elevation and the nozzle installation up the hillside in such a manner that the piping will drain back to the sump when the pump is not operating.

The type of soil influences to a great extent the volume of water that can be discharged to it. Clay soil, of course, does not absorb water as rapidly as loose loam or gravel soil. The clay soil is also susceptible to poisoning by the effects of sodium in the waste. The clay soil has the property of acting as a zeolite and will exchange calcium normally present in clay soil for sodium. If the clay soil becomes loaded with sodium, it loses the property of absorbing water and becomes exceedingly hard to the point where no vegetation will grow. If this happens, the spray irrigation field is ruined. The limits for sodium which have been suggested are 100 parts per million. On clay soils, it is recommended that the spray field be given an occasional treatment with agricultural lime in order to compensate for the effects of the sodium in the waste.

The type of vegetation has some importance in determining the water absorbing characteristics of the soil. Our experience has been that grasses are most satisfactory for dairy wastes. Reed's canary grass has been recommended as being the best cover crop. However, we have had good success with canary grass and orchard grass. It is believed that the difference in the grasses is relatively minor and the most important thing is that a good cover crop be obtained. Our experience has been that in starting with a bare field, it takes approximately two years to obtain a good cover crop to obtain maximum absorption of the waste. If possible, a field already planted in grass is the most desirable one to obtain.

The subject of winter operation is always of interest in discussing spray irrigation systems. The plant at Shirley, Indiana has operated throughout the winter for three years and has not encountered any extreme difficulties during that period. Some trouble has been experienced with frozen nozzles. However, the best remedy has been found to be to remove the nozzle and allow it to thaw out indoors. During this period other nozzles can be used. During the extreme cold weather the waste freezes on the ground and does not appear to run off to any great extent. The most difficult period for operation of this system appears to be in March when there are periods of alternate thawing and freezing. During this time there will be run-off from the field which will contain incompletely treated waste. During this period the field is normally saturated with water due to melting snow and, since the grass has not started to grow, there is little chance for purification. Some of the waste is absorbed into the ground even under these conditions and the waste, in passing over the ground, receives some treatment so that wastes reaching the water course are considerably less objectionable than the raw wastes from the factory. This period appears to last only about a month and as soon as the grass begins to grow, the run-off ceases.

The spray irrigation system has been found the most satisfactory from an operational point of view of any method of cheese factory waste disposal. As you no doubt know, in cheese factories the whey which is produced is a by-product having a very low value. In normal operation a certain amount of whey is discharged to the sewer and, under some conditions, a substantial amount of whey may reach the sewers. The whey is nutritionally unbalanced in that it is deficient in protein and nitrogen. Accordingly the bacteria which normally operate in a conventional

waste treatment system do not have sufficient nitrogen to completely oxidize the waste material. The result is inefficient operation of the conventional waste treatment plant. In the case of spray irrigation, this difficulty is not nearly as prevalent. The soil contains nitrogen to provide for the decomposition of considerable amounts of whey and since the nitrogen is only borrowed and returns to the soil, the system seems to operate more or less indefinitely. Our experiences indicated that a spray irrigation system will operate successfully with considerably more whey in the waste than can be tolerated in a trickling filter or aeration plant. If large amounts of whey are discharged to the spray irrigation system, it does not appear to effect the grass and the tendency is for weeds to grow in the place of the grasses. This appears to be because the weeds can thrive on less nitrogen than grasses.

At the present time, Kraft Foods Company has 10 installations of waste disposal systems by use of spray irrigation at cheese factories. The installations have been made at plants where we have had considerable trouble and controversy regarding waste disposal problems for many years.

In conclusion, it has been our experience that the spray irrigation type of treatment has eliminated the operating problems associated with the usual sewage treatment methods, that it requires less attention by the plant personnel, that it improves the soil as pasture land, and that, in most cases, it has created sufficient interest among plant personnel so that satisfactory operation of the system has been obtained.

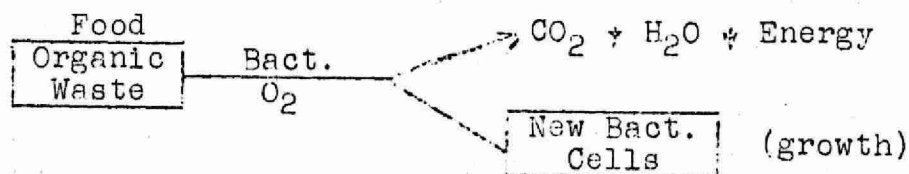
RELATIONSHIP OF INORGANIC NUTRIENTS, SYNTHETIC ACTIVITY
AND PURIFICATION RATE IN BIOLOGICAL PROCESSES

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Nutrition and Synthesis

The subjects nutrition and synthesis are so intimately related that it would be difficult to discuss either adequately without borrowing heavily from the other. Aerobic biological treatment methods had been applied to waste waters, largely domestic sewage, for at least 40 years before any serious consideration was given to nutrition or synthesis. The issue was forced upon us when industrial wastes of wide variety and character were accepted for treatment in municipal systems or attempts were made to treat them separately by biological means.

At the present time, it is generally conceded that the removal of organic pollutants from waste waters is accomplished primarily by bacteria and that rapid removal depends upon unrestricted reproduction or growth (synthesis) of the bacteria while using a minimum amount of the organic pollutant (food) for energy. This condition is illustrated as follows:



On the basis of current knowledge, the greatest yields of new growth are produced when the organic waste is properly balanced, nutritionally. Furthermore, the product formed under such conditions has maximum nutritive value which is an important consideration. As long as domestic sewage is involved the product will be relegated to use as fertilizer of relatively low sale value. However, with a number of industrial wastes the product may be used for animal or, possibly, human foodstuffs with high sale value. Fodder yeast is currently being produced from waste sulfite liquor and serious attempts are being made to modify its character so that it will be acceptable as human food. Other wastes of acceptable aesthetic quality are being treated biologically to produce foodstuffs to meet the demands of increasing populations (3). It is conceivable that other bacterial growths may be used for such purposes. In anticipation of that eventuality, it would seem wise to reserve the term "sludge" for biological growths not destined to be used for food purposes.

The discussions which follow with respect to nutrition and synthesis apply to the activated sludge process since it has lent itself most favorably to such research. There is good theoretical reason and some experimental evidence to support its application to high rate trickling filters.

Nutrition

Bacteriologists have long been aware of the nutritional needs of a great many organisms. These range from autotrophs with only inorganic requirements through a spectrum of heterotrophs with a wide variety of needs. In general, however, where mixed cultures are used for initial seeding purposes those organisms which can utilize the available organic matter most efficiently, i.e., reproduce most rapidly, will predominate, providing adequate sources of mineral elements are present. Nitrogen, phosphorus and sulfur are considered to be the elements needed in measureable amount. The former should be present as NH_4 , the phosphorus as PO_4 and the sulfur as SO_4 . Usually, the carriage water can be relied on to supply the small amounts of sulfate needed. Trace amounts of magnesium, potassium, calcium, iron, manganese, zinc, copper and cobalt are probably essential for most bacteria (12). The carriage water is normally relied upon to furnish these.

The current interest in the nutritional aspects of waste treatment may be considered to have stemmed from difficulties encountered in the measurement of 5-day B.O.D. using distilled water buffered with sodium bicarbonate for dilution purposes. Eldridge (2) had encountered variable B.O.D. values in different dilution of a beet sugar waste and had attributed the trouble to variations in the amount of sewage seed in the bottles. Holderby and Lea (8) performed studies to show that results similar to those obtained by Eldridge could be caused by varying the carbon to nitrogen ratio. Nichols and Lea (11) reported that B.O.D. dilution water should contain sufficient ammonia nitrogen to insure a B.O.D. to nitrogen ratio of 16 to 1 and a B.O.D. to phosphorus ratio of 400 to 1. The latter was modified by Lea as a result of later studies to 40 to 1 (10).

Excess Nitrogen

The writer first became interested in the nutrition of activated sludge when in a study of sludges obtained from different municipalities it was noted that some were incapable of nitrification. Further study showed that the ability for nitrification was a function of the carbon to nitrogen ratio in the feed to which it was accustomed, more commonly referred to in the waste treatment field as the B.O.D. to nitrogen ratio. Sewages having excessive amounts of nitrogen, with less than 16 parts of B.O.D. for each part of nitrogen, gave sludges with increasing capacity for nitrification as the ratio of nitrogen increased. On the other hand, at B.O.D. to nitrogen ratios of 16 or more to one, nitrification became extinct (14).

Many industrial wastes, for example animal packing house and tannery wastes, contain nitrogen in excess of that required in stabilization by activated sludge, consequently nitrification and attendant problems are often a matter of concern (15).

Mineral Requirements

It has been recognized for several years that many industrial wastes are poorly balanced from a nutritional viewpoint. Early studies with sulfite waste liquor, which is notoriously deficient in both nitro-

gen and phosphorus, showed that the rate of removal of B.O.D. was hastened greatly in the presence of adequate amounts of nitrogen and phosphorus (16). Subsequent studies with other materials including sugars established the fundamental need for both nitrogen and phosphorus (17).

The need for nitrogen and phosphorus may be satisfied in either of two ways. Domestic sewage normally contains these mineral elements in excess. Therefore, it may serve as a source of such nutrients for wastes requiring supplementation. The addition of industrial wastes to municipal sewer systems is common practice, consequently it often becomes important to know what nutrients are needed and how much in order to make sure that the ability of the sewage to supply the needs is not exceeded. Where admixture with adequate amounts of domestic sewage is not possible, it often becomes necessary to add inorganic sources of nitrogen and/or phosphorus. Since this constitutes a continual expense a knowledge of the amounts required is important.

Requirements for Mixtures with Domestic Sewage

The requirements during treatment in combination with domestic sewage have often been referred to as "Maximum requirements" and have been determined by investigations on mixtures in which the industrial waste was varied to produce effluents with and without excess nitrogen and phosphorus (5). Mineral requirements were determined at 10, 20 and 30 C using two methods of calculation: 1. by differences in influent and effluent analyses and 2. by measuring the amount of mineral nutrient contained in the sludges wasted to maintain uniform aeration solids concentration (1500 ppm.).

The results of the studies made on mixtures with domestic sewage are shown in Tables I and II. The optimum B.O.D. to N ratio varied from 13 to 1 to as high as 26 to 1, with 6 of the nine values ranging from 16 to 19 of B.O.D. to 1 of nitrogen. In other words, the nitrogen requirements varied from 3.8 to 7.7 lbs. per 100 lbs. of 5-day B.O.D., with 6 of the 9 values falling in the range of 5.3 to 6.2 lbs. Temperature appeared to have no consistent effect.

The B.O.D. to P ratios varied from 67 to 1 to as high as 195 to 1, with 6 of the 9 values falling in the range of 83 to 102 of B.O.D. to 1 of P. On a weight basis, from 0.51 to 1.49 lbs. of P were used per 100 lbs. of 5-day B.O.D. with 6 of the 9 values falling in the range of 0.82 to 1.20 lbs. Again, temperature appeared to exert no consistent effect.

From these studies it appears that a B.O.D. to N ratio of about 17 to 1 and a B.O.D. to P ratio of about 100 to 1 are optimum for stabilization of such wastes in combination with domestic sewage. The value for nitrogen is in good agreement with results previously obtained by the writer using sulfite waste liquor (16) and those relating to nitrifying and non-nitrifying sludges (14). The value for phosphorus, however, is somewhat less than the 45 to 1 ratio obtained with sulfite waste liquor.

Requirements in the Absence of Significant Amounts of Domestic Sewage

Helmert, et al (6) have reported on studies made with cotton kierung, rope kierung and brewery wastes while the nitrogen of the mixture was varied over a wide range. The phosphorus was added in excess in all cases. Usually the maximum level of nitrogen added was in slight excess. The results are shown in Tables III and IV. Under such conditions of study, a great variation of B.O.D. removals resulted, consequently it was necessary to evaluate the nutrient requirements in terms of the B.O.D. removed. The data shown would suggest that as little as 1.1 lb. of nitrogen and 0.19 lb. of phosphorus would suffice for the removal of 100 lb. of B.O.D. It should be noted that B.O.D. removals accomplished on such limited nutrients were unsatisfactory in the established aeration time.

Helmert, et al (6) have pointed out that other factors such as the settling character of the sludge and, possibly, filterability will determine in large degree the amount of nutrients needed. This is a matter which will be decided in each case. However, the data do indicate the maximum requirements would range from 3.7 to 5.5 lbs. of nitrogen and from 0.49 to 1.24 lbs. of phosphorus for each 100 lbs. of B.O.D. removed. These values are in fair agreement with those obtained in combination with domestic sewage.

A summary of nitrogen and phosphorus requirements as determined in the presence of domestic sewage and by supplementation is shown in Table V.

Operational Variables Affecting Nutritional Requirements

Among the more important variables which occur in the operation of biological treatment units are the aeration solids concentration, B.O.D. loading and temperature. The effect of these variables on nitrogen requirements was studied by Weinberger (20) using a synthetic waste of highly reproducible character.

The effect of varying the aeration solids concentration over the range of 500 to 2500 ppm. is shown in Figure 1. The nitrogen requirement decreased with increasing aeration solids for a given B.O.D. loading. Figure 2 shows the effect of increased B.O.D. loadings when using several different aeration solids concentrations. Nitrogen requirements diminished rapidly as B.O.D. loadings decreased and increased to a maximum of about 5 lbs. per 100 lbs. of B.O.D. regardless of the aeration solids concentration. The current trend is to express B.O.D. loadings in terms of lbs. of B.O.D. fed per day per lb. of aeration solids carried in the system. When the data of Figure 2 are recalculated on this basis, we obtain the data shown in Figure 2A. This demonstrates that nutrient requirements increase with B.O.D. loading up to about 0.4 lb. of B.O.D. per lb. of aeration solids and that requirements are about 5 lb. of nitrogen per 100 lb. of B.O.D. at higher loadings.

Temperature is another factor which must be reckoned with as is demonstrated in Figure 3. This would indicate the nutrient requirement during high temperature operation would be materially decreased. Helmer's data did not show this trend, presumably because of the higher B.O.D. loadings which he used.

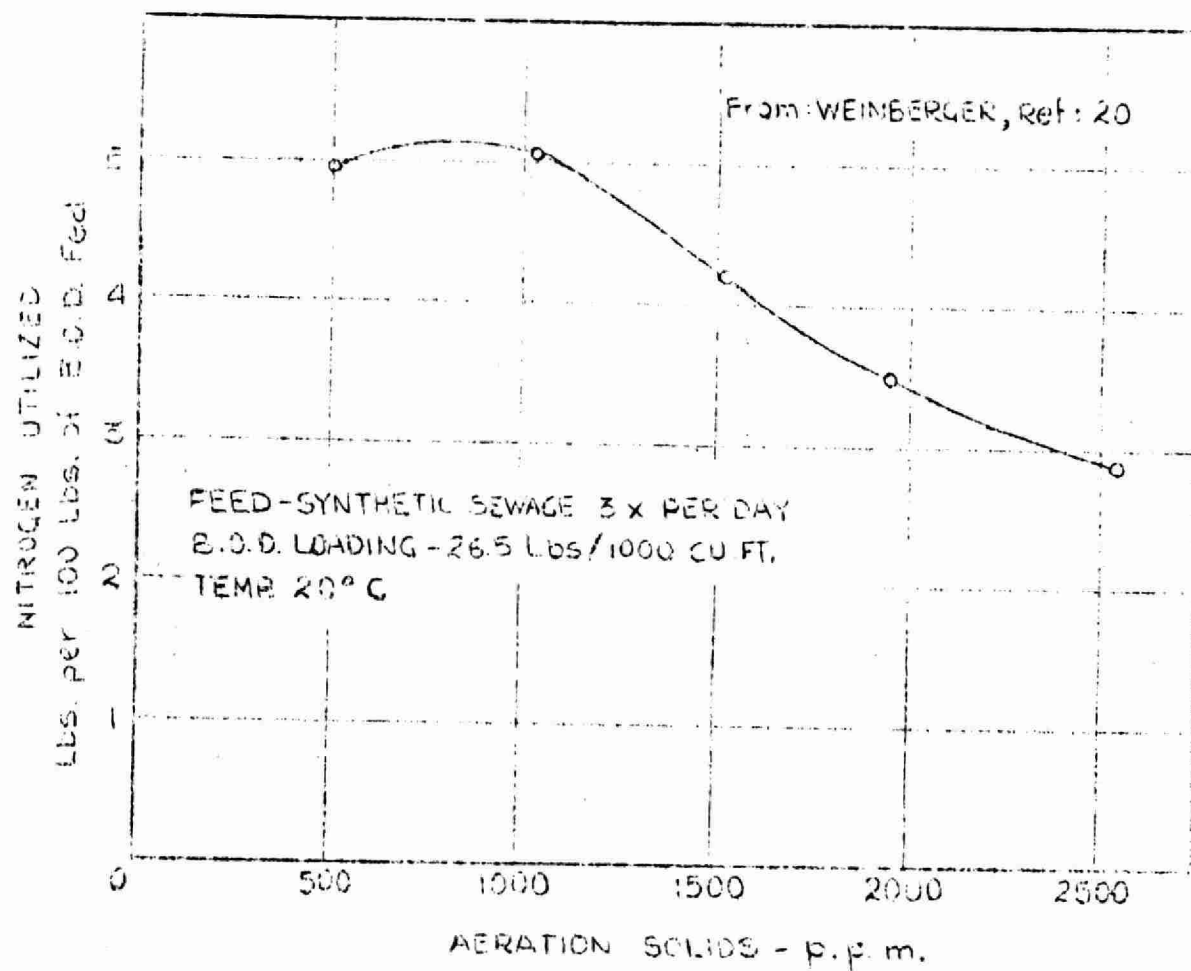


FIGURE 1 - NITROGEN UTILIZATION VERSUS
AERATION SOLIDS

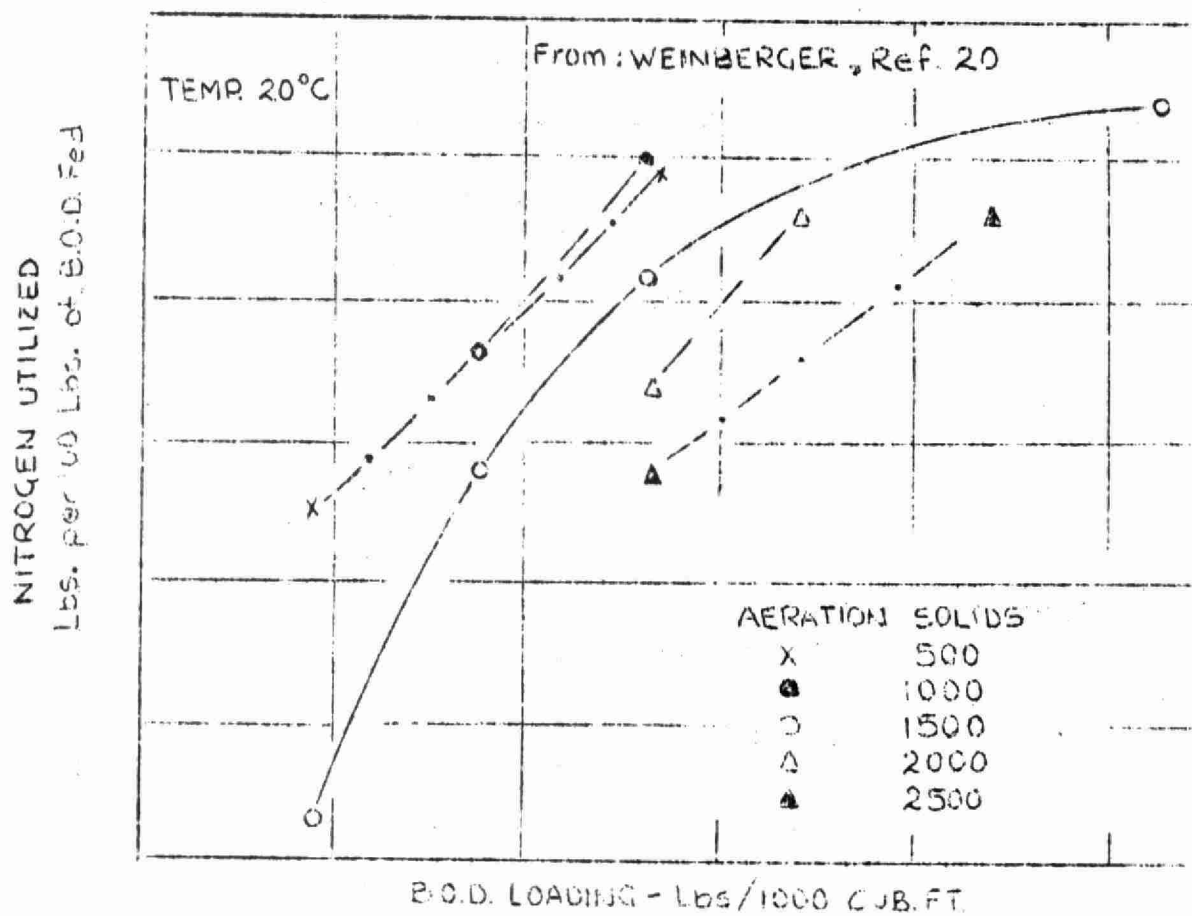
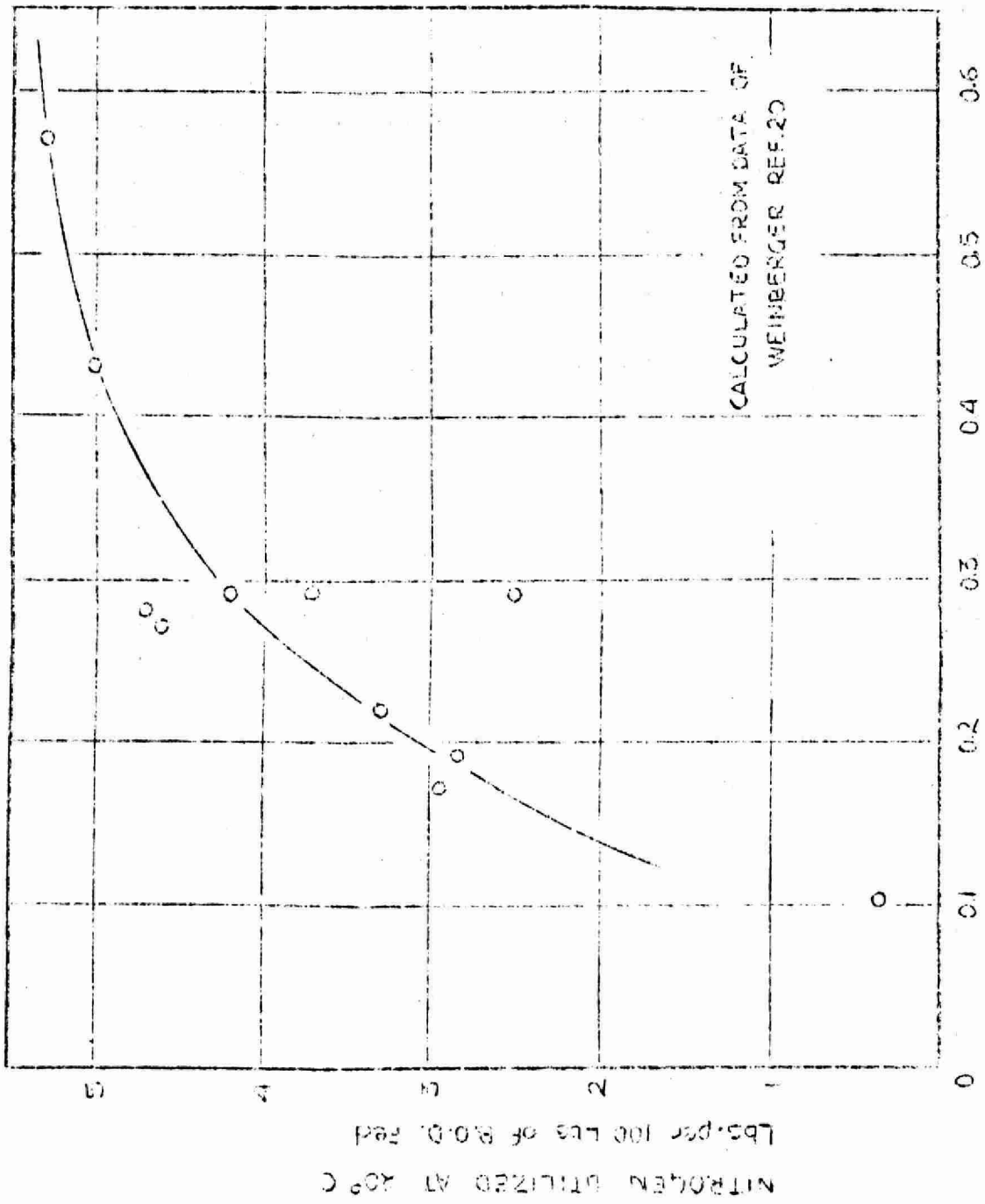


FIGURE 2 - NITROGEN UTILIZATION VERSUS B.O.D. LOADING



Lbs. B.O.D. APPLIED/DAY/LB. AERATION SOLIDS

FIGURE 2A NITROGEN REQUIREMENTS VERSUS B.O.D. LOADING

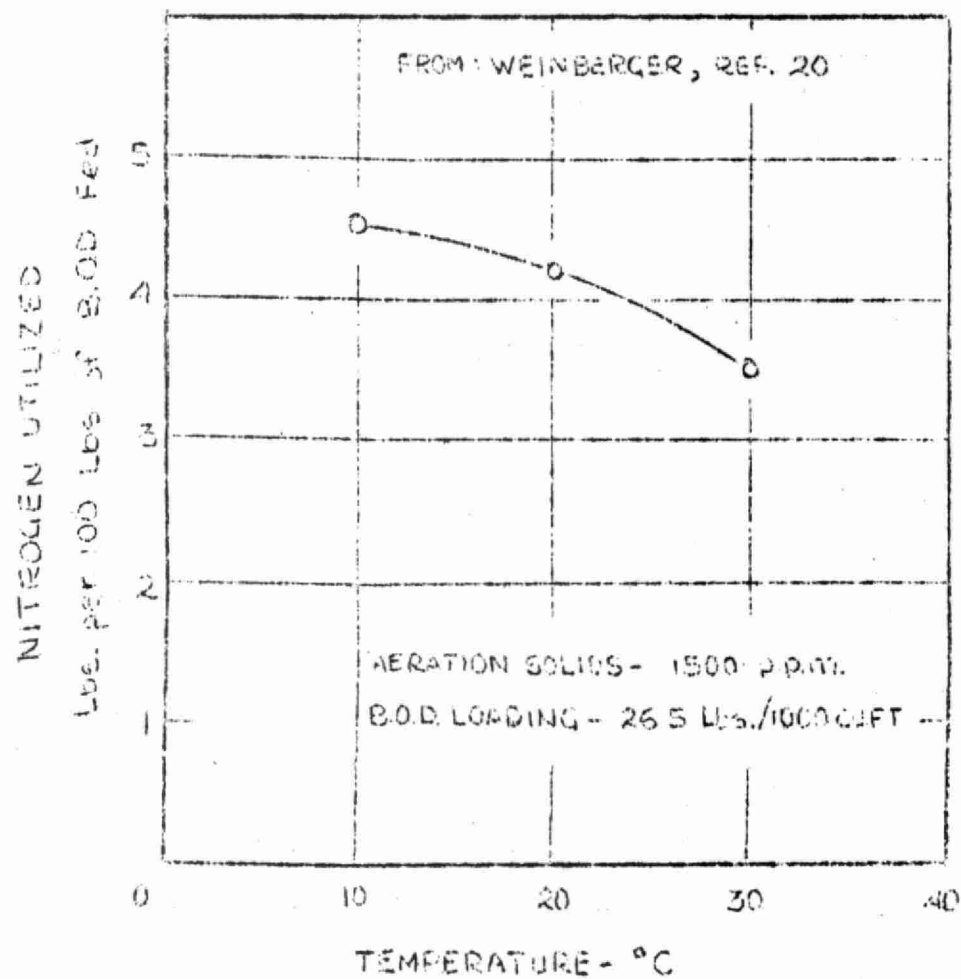


FIGURE 3 - NITROGEN UTILIZATION VERSUS TEMPERATURE

Synthesis or Growth

One of the fundamental characteristics of all living matter is that of reproduction, for without it any species will perish. In order for reproduction to occur, synthesis of new cell tissue must take place which is like that of the parent cells so that the characteristics of the species will be maintained even unto the N^{th} generation.

The sole requirements for synthesis are the presence of living organisms, available food supply and proper environment. A certain amount of food is needed to supply energy for endogenous respiration but this requirement for healthy organisms is very low. As the food supply is increased above that needed for endogenous respiration, a source of energy and raw materials becomes available for reproduction. At any given temperature, the rate at which reproduction will occur will depend upon the amount of available food at any instant and the rate of replenishment. The rate of reproduction will increase with the level of the available food supply until the minimum generation time of the organisms becomes the limiting factor. This limiting rate of reproduction is a real factor in activated sludge treatment, where the aeration solids or population of active organisms is held constant and in trickling filters because of the more or less uniform surface area exposed to the food supply. The writer's concept of food supply - synthesis relationships during biological treatment is shown in Figure 4.

From Figure 4 it may be reasoned that any considerations concerning growth of sludge during biological stabilization of organic matter should be based upon food supplies considerably in excess of those needed to satisfy the basal metabolic needs. Furthermore, the supply should not be so great that appreciable amounts remain in the effluent. A second item concerns the matter of terms in which to express the food supply on a quantitative basis. Where studies have been conducted with substrates containing known substances, the practice has been to relate growth on a weight basis to the weight of food material. In situations where the composition of the food supply was uncertain or of a mixed nature, such as in many industrial wastes, the practice has been to relate growth to the 5-day B.O.D. Therefore, in attempting to evaluate synthesis or growth, it is important that the comparisons be made from data obtained with relatively high food supply (B.O.D. loading) and that attention be given to the mode of expressing the food supply.

Growth Studies with Substrates of Known Composition

A great deal of information has been accumulated concerning microbial assimilation of organic matter. A review of the existing knowledge was made by Clifton in 1946 (1). However, such information is, probably not directly applicable to the waste treatment field because of the mass inoculations which are used in the latter.

A number of investigators have made studies of synthesis or growth using activated sludge to stabilize substrates of known composition. Considerable information also exists concerning the conversion of sugars to yeast under aerobic conditions. A summary of data obtained from several sources is shown in Table VI. From the reported results it can be concluded that the nature of the substrate controls the

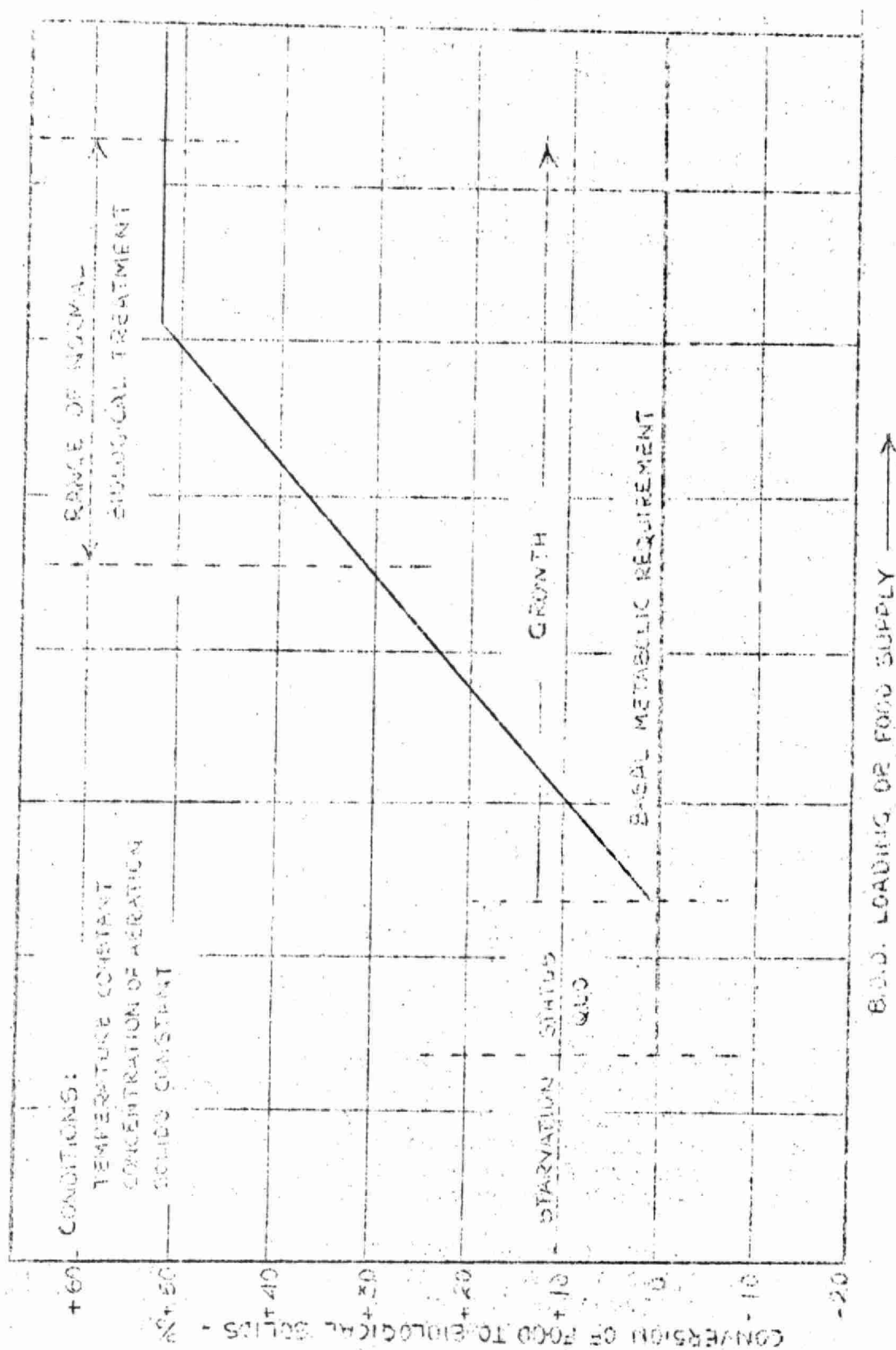


FIGURE 4 - FOOD SUPPLY - SYNTHESIS RELATIONSHIPS IN BIOLOGICAL TREATMENT

oxidative - assimilative relationships to a considerable degree. Yields of new growth in the range of 50 to 60 per cent of the dry weight of the organic food can be expected.

Growth Studies Obtained with Industrial Wastes

Several investigations have been made of the amount of growth obtained when feeding industrial wastes. Due to the uncertain and complex character of the wastes, all the investigators have correlated the growth obtained with the 5-day B.O.D. of the waste. The writer (16) in studies with sulfite waste liquor found the amount of growth to be in almost direct proportion to the B.O.D. of the waste as fed. A yield of about 1 lb. of dry sludge for each lb. of 5-day B.O.D. was indicated.

Helmers, et al (6) conducted growth studies on cotton kliering, rag-rope kliering and brewery wastes, also on peptone and glucose. Their results showed phenomenally uniform growth regardless of the substrate used. Typical data are shown in Figures 5 and 6. At B.O.D. loadings of 70 lbs. per 1000 cu. ft. per day, from 37 to 42 lbs. of new sludge were produced each day. This corresponds to a conversion factor ranging from 0.53 to 0.60.

Gellman and Heukelkian (4) have reported on studies of sludge growth during biological purification of jute cook liquor, yeast waste, gum waste and boardmill white water. A summary of their data is shown in Figure 7 and shows a yield of about 0.5 lb. of volatile solids in new sludge growth per lb. of 5-day B.O.D. fed, with no apparent divergence from a straight line relationship over a wide range of B.O.D. loadings. These findings are in excellent agreement with those reported by Helmers, et al (6), when their results are corrected to a volatile solids basis.

Heukelekian, et al. (7) have reported on some extensive growth studies using several sewages, largely domestic in origin, having appreciable amounts of suspended solids in relation to the B.O.D. Their data showed definite reductions in sludge growth as the aeration solids increased. This same trend was noted by the writer in some studies on domestic sewage, also (18). Heukelekian has offered the following formula for calculating sludge growth in such wastes:

$$A = 0.055 S \div 0.5B$$

where A is the lb. of volatile suspended solids accumulation per day, S is the lb. of volatile mixed liquor suspended solids, and B is the lb. of B.O.D. fed per day. The need for a correction factor based upon the suspended solids in the aeration mixture indicates that sludges produced from domestic sewage are somewhat different in character from those produced on industrial wastes in which the major part of the B.O.D. is in soluble form.

The writer (18) has shown that net growth of activated sludge depends upon temperature as well as other factors.

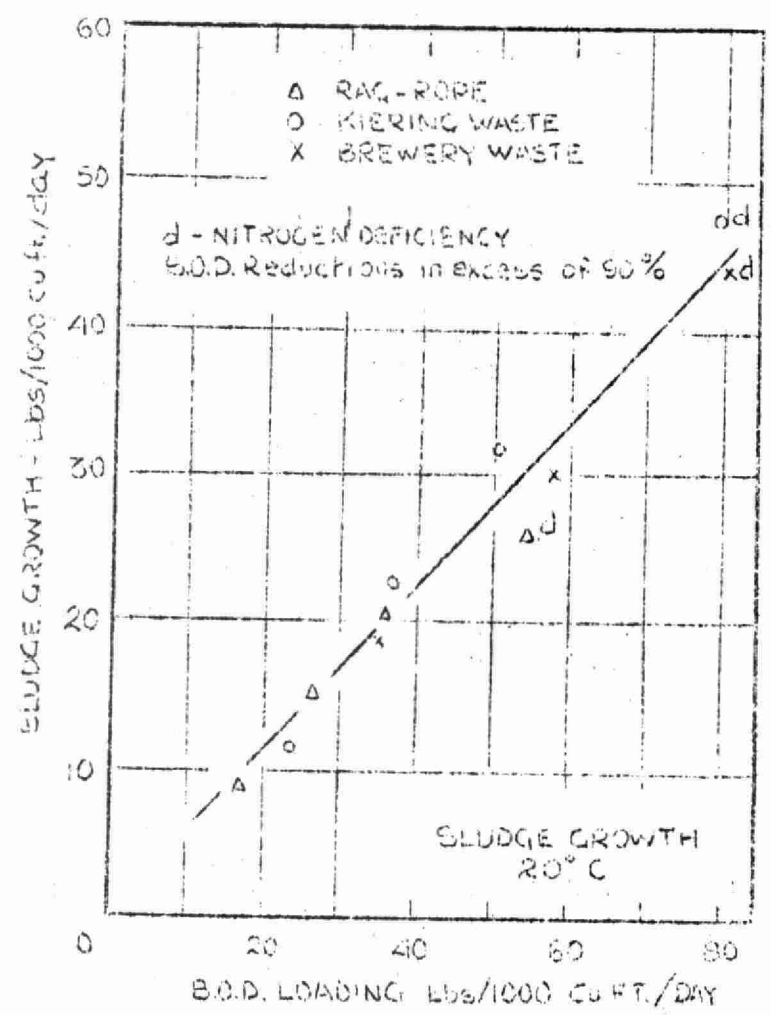


FIGURE 5 - SLUDGE GROWTH VERSUS
B.O.D. LOADING AT 20°C

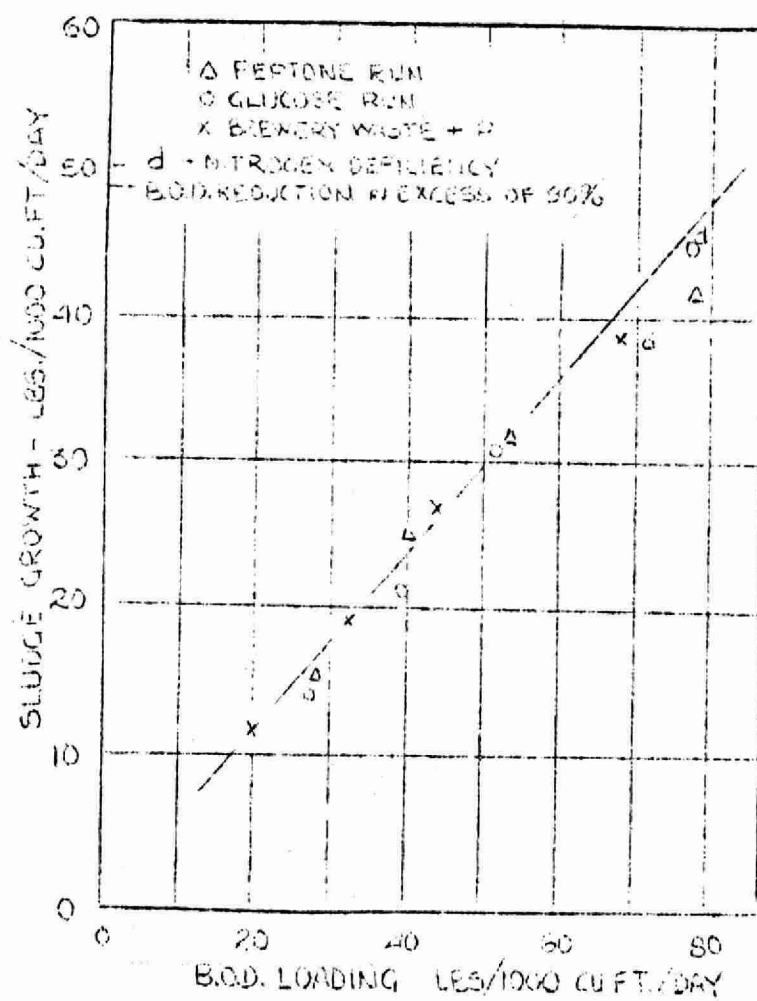
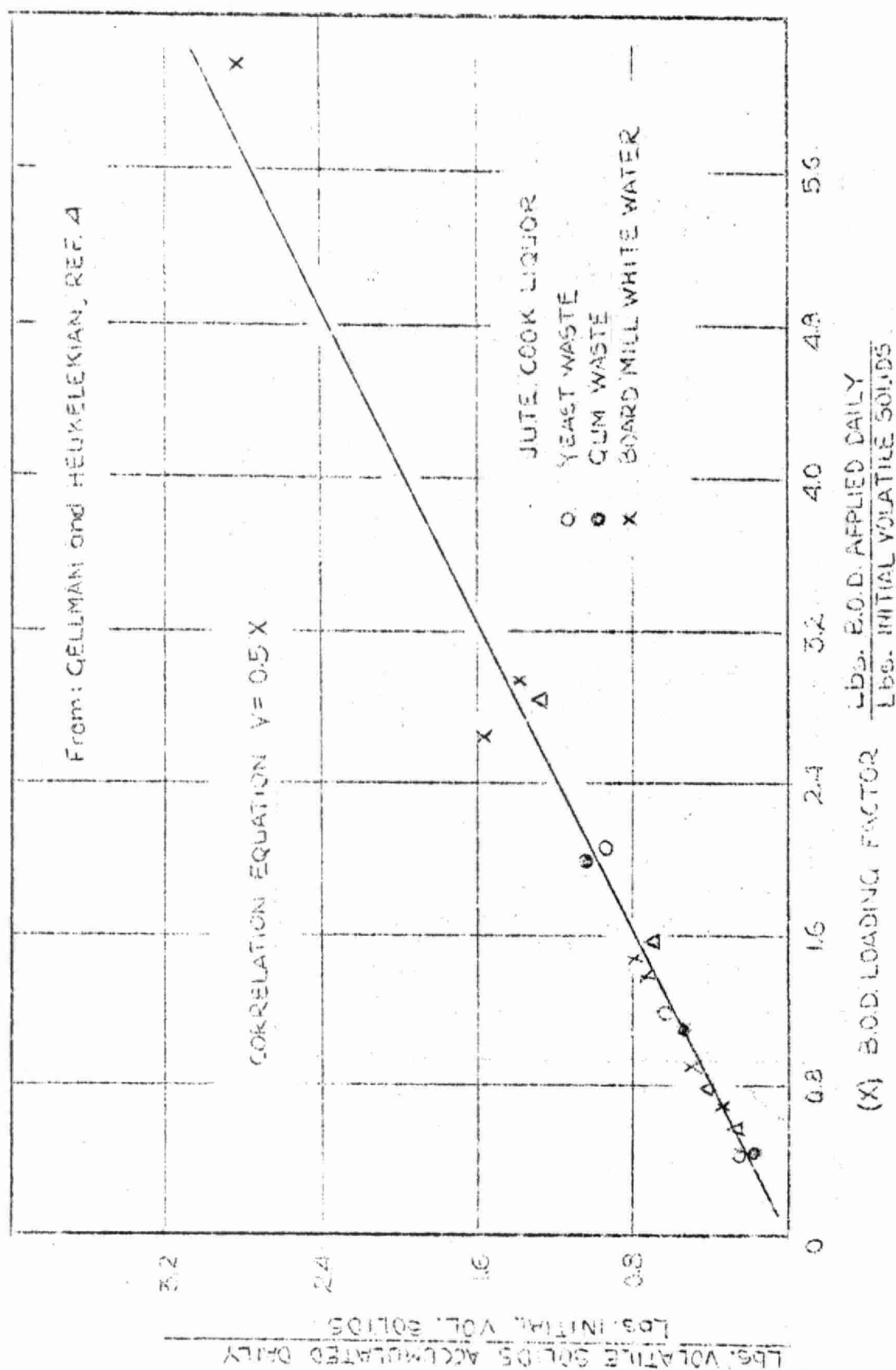


FIGURE 6 - SLUDGE GROWTH VERSUS
B.O.D. LOADING AT 25° C.



Discussion

From the information already presented on growth, it is quite definite that the amount of growth can be predicted from the 5-day B.O.D. Now, if the composition of the sludge growth were uniform it would be a simple matter to calculate the nutritional requirements.

It is axiomatic that reproduction through synthesis is necessary for the preservation of a species. It is also axiomatic that, if the species is to maintain its original character, it must be built of identical materials. Thus, the nutritional requirements can be estimated from an analysis of the dead material. A great deal of such study has been made on pure cultures of organisms, animals and plants. A great variation in composition of the many species occurs and, consequently, it is difficult to select representative values which might depict the condition in mixed cultures common in waste treatment.

Hoover and Porges (9) have analyzed an activated sludge produced in stabilizing skim milk solids for carbon, hydrogen, oxygen, nitrogen and ash. Their sludge contained 11.27 per cent nitrogen and, on the basis of their analyses, they have calculated an empirical formula of $C_5H_7NO_2$. Phosphorus, however, is an element which is present in bacterial cells and yeasts in macro amounts. The data given by Helmers, et al. (5) (6) shows a mean of 1.02 per cent of phosphorus and 8.0 per cent of nitrogen in the activated sludges developed on the various industrial wastes. Using these values as a basis of calculation the empirical formula $C_{118}H_{170}O_{51}N_{17}P$ is indicated. If the phosphorus is ignored, a formula $C_7H_{10}NO_3$ is obtained. From the wide variation of nitrogen in the activated sludges reported by Helmers, it does not seem reasonable to compose a definite empirical formula for activated sludge. Therefore, even though the amount of growth can be predicted quite closely, the amount of mineral elements needed cannot.

Critical Nitrogen Levels

The data presented by Helmers, et al. (6) show that the nitrogen content of the sludges produced decreases as the amount of available nitrogen per unit of B.O.D. decreases. Their data also show that satisfactory B.O.D. removals can be obtained with small deficiencies of nitrogen. When the deficiencies become too great the sludges tend to have poor settling and filtering characteristics. Helmers has suggested that a minimum of 7 per cent of nitrogen should be present in the volatile portion of the sludge to maintain desirable qualities. On the basis of this information and B.O.D. - growth relationships, the following formula may be used for calculating the acceptable minimum nitrogen requirements:

Minimum - N = (5-day B.O.D. x 0.5) x .07 x fraction of Vm in sludge
where Minimum - N will be expressed in the same terms as the B.O.D.

Critical Phosphorus Levels

The data on minimum amounts of phosphorus needed to supply metabolic requirements during biological treatment is very limited.

The studies reported by Helmers indicate the activated sludges to contain from 0.74 to 2.25 per cent, when phosphorus was in excess. Thus, from 90 to 270 lbs. of B.O.D. were stabilized per lb. of phosphorus used. Why the phosphorus requirements appear to vary so much is not known. There is some evidence that it may be related to pH or possibly the Ca^{++} concentration of the substrate.

In view of the important role of phosphorus in various enzyme systems, it would appear prudent to allow at least 1 lb. of phosphorus for each 150 lbs. of 5-day B.O.D. until experience indicates that lesser amounts will satisfy the needs in a particular situation. Greenberg, et al. (21) have shown a phosphorus requirement of 0.44 lb. per 100 lb. of B.O.D. Their data were obtained at a loading of 0.17 lb. of B.O.D. per lb. of aeration solids. From Figure 2A, it will be noted that the nitrogen requirement at corresponding loading was about 50 per cent of that obtained at higher loadings. Therefore, it would seem reasonable to conclude that Greenberg would have found a phosphorus requirement of about 0.88 lb. per 100 lb. of B.O.D. under high loading rates.

Available Nitrogen

Only that nitrogen which is present as NH_4^+ can be counted upon as being 100 per cent available. Nitrogen in the form of urea may become 100 per cent available but only after hydrolysis by enzymes. Although many bacteria elaborate the enzyme, urease, the rate of hydrolysis at low temperatures, 10°C . range, is slow and may not keep pace with bacterial requirements (20).

Helmers, et al (5) have studied the availability of nitrogen from various organic sources. They report values ranging from 30 to 70 per cent depending upon the source, the temperature, and other variables. For estimating purposes a value of 50 per cent may be used and adjustments made later, based upon experience.

Summary

Nutrition and synthesis are intimately related factors. Synthesis and growth are essentially synonymous terms. Growth results from the marshalling of part of the food supply and accessory mineral factors to produce new generations of the organisms with characteristics and chemical composition similar to the progenitors. A considerable fraction of the food is used for energy purposes.

Growth or synthesis can be predicted from the 5-day B.O.D. of a waste. About 0.5 lb. of new growth will occur for each lb. of B.O.D. stabilized, in normal activated sludge operation.

$$\text{Growth} = 0.5 \text{ (5-day B.O.D.)}$$

When appreciable suspended solids of organic nature are present in the waste, such as domestic sewage, a negative correction factor must be applied.

Nitrogen and phosphorus are necessary mineral elements which often have to be supplied because of deficiencies in the waste. Where

it is desirable to produce a biological growth or activated sludge with maximum nitrogen and phosphorus content; the following 5-day B.O.D. to mineral nutrient ratios are indicated:

B.O.D. to N = 17 to 1

B.O.D. to P = 90 to 1

Where it is desired to accomplish rapid stabilization of a waste with minimum amounts of mineral nutrients, the following ratios are indicated:

B.O.D. to N = 32 to 1

B.O.D. to P = 150 to 1

Mineral nutrient requirements can be greatly reduced by keeping B.O.D. loadings per lb. of aeration solids at very low levels, in the range 0.1 lb. This may be accomplished by carrying extremely high aeration solids in conventional sized tanks or by providing several times the normal aeration tank capacity.

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TABLE I

MAXIMUM NITROGEN REQUIREMENTS DURING ACTIVATED SLUDGE STABILIZATION OF
INDUSTRIAL WASTES

Waste	<u>B.O.D. Ratio</u> <u>N</u>			Lbs. Nitrogen Per 100 Lbs. 5-Day B.O.D.		
	10°C	20°C	30°C	10°C	20°C	30°C
Cotton Kiering	18	16	16	5.6	6.2	6.2
Rag-Rope Mixture	26	13	17	3.8	7.7	5.9
Brewery	17	22	19	5.9	4.6	5.3

TABLE II

MAXIMUM PHOSPHORUS REQUIREMENTS DURING ACTIVATED SLUDGE STABILIZATION
OF INDUSTRIAL WASTES

	<u>B.O.D. Ratio</u> <u>P</u>			Lb. Nitrogen Per 100 Lbs. 5-Day B.O.D.		
	10°C	20°C	30°C	10°C	20°C	30°C
Cotton Kiering	102	83	90	0.98	1.20	1.11
Rage-Rope Mixture	189	122	195	0.53	0.82	0.51
Brewery	99	91	67	1.01	1.10	1.49

TABLE III

NITROGEN REQUIREMENTS OF INDUSTRIAL WASTES DURING ACTIVATED SLUDGE TREATMENT

Waste	Supple- mental N ppm	Lbs. Nitrogen per 100 lbs. 5-day B.O.D. Removed		
		10°	20°	30°
Cotton Kiering	0	2.0 (83)	2.5 (89)	2.3 (91)
	2	2.6 (84)	3.5 (91)	2.8 (91)
	4	3.3 (86)	4.3 (95)	3.5 (93)
	6	3.6 (88)	5.5 (95)	4.2 (94)
Rope Kiering	0	--- (50)	--- (50)	1.1 (72)
	8	1.7 (60)	1.8 (75)	2.0 (83)
	15	3.1 (74)	2.3 (82)	2.5 (91)
	25	4.3 ¹ (80)	3.7 ¹ (87)	3.6 ¹ (92)
Brewery	0	1.5 (70)	1.8 (94)	1.2 (94)
	5	2.3 (82)	2.8 (95)	1.6 (96)
	15	3.8 (93)	4.8 (97)	4.4 (95)
	25	4.3 ¹ (88)	4.9 ¹ (98)	4.4 ¹ (95)

¹ Considered to represent maximum values because of excess nitrogen in effluents.

TABLE IV
PHOSPHORUS REQUIREMENTS OF INDUSTRIAL WASTES DURING ACTIVATED SLUDGE
TREATMENT

Waste	Supple- mental N ppm	Lbs. Nitrogen per 100 lbs. 5-day B.O.D. Removed		
		10°	20°	30°
Cotton Kiering	0	.31 (83)	.44 (89)	.43 (91)
	2	.44 (84)	.53 (91)	.44 (91)
	4	.44 (86)	.54 (95)	.50 (93)
	6	.44 (88)	.54 (95)	.54 (94)
Rope Kiering	0	--- (<50)	--- (150)	.19 (72)
	8	.40 (60)	.45 (75)	.35 (83)
	15	.52 (74)	.44 (82)	.45 (91)
	25	.68 ¹ (80)	.57 ¹ (87)	.49 ¹ (92)
Brewery	0	.60 (70)	.65 (94)	.57 (94)
	5	.87 (82)	.89 (95)	.68 (96)
	15	1.00 (93)	1.21 (97)	1.20 (95)
	25	1.09 ¹ (88)	1.24 ¹ (98)	1.07 ¹ (95)

¹Values obtained in presence of excess nitrogen

TABLE V
SUMMARY OF NUTRIENT REQUIREMENTS

Mineral Nutrient	Method	Lbs. per 100 Lbs. B.O.D. Removed	
		Range	Mean
Nitrogen	With Sewage	3.8-7.7	5.9
	By supplementation	3.7-5.5	4.3
Phosphorus	With Sewage	0.51-1.49	1.01
	By Supplementation	0.49-1.24	.57

TABLE VI
CONVERSION OF KNOWN ORGANIC MATERIALS DURING
BIOLOGICAL TREATMENT

Substance	Organisms	Per Cent Conversion to New Growth	Reference
Carbohydrate	Act. Sludge	62-85	(13)
Alcohols	" "	52-66	"
Amino Acids	" "	32-68	"
Organic Acids	" "	10-60	"
Skim Milk Solids	" "	50-52	(9)
Glucose	Yeast	49-59	(19)
Glucose	Act. Sludge	44-64	(17)
Sucrose	" "	58-68	"

INDUSTRIAL WASTE TREATMENT IN MICHIGAN

Dr. C. Fred Gurnham

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East Lansing, Michigan

In speaking to you today on the subject of industrial waste treatment in Michigan, I am presuming on two entirely unrelated facts. I am interested in the treatment and control of wastes from industry, and I am a resident of Michigan. These two qualifications apply equally well, or better, to the people of our State Water Resources Commission. One of them, rather than I, should be presenting this paper.

As a college professor, however, I have neither the desire nor the intention of giving up this opportunity to talk to a captive audience. I must admit, though, that I have received a great deal of assistance from the Water Resources Commission in the preparation of this paper, and am especially indebted to Milton P. Adams, the Executive Secretary, and Loring F. Oeming, Sanitary Engineer. You must not hold these men responsible, however, for any of my statements, since this paper was finally assembled in a manner quite different from our discussions.

Because of these relationships, I am not prepared to give you a statistical survey of the treatment plants constructed or of the polluted streams brought under control. I doubt that you would be interested in such a tabulation. Instead, I shall select several of the industrial waste control measures that appeal to me because of their newness or novelty, and that I believe may interest the industries of Ontario.

Material Salvage and By-Product Recovery

In the control of pollution from industrial wastes, treatment operations are not nearly as economical as are measures to eliminate waste in the manufacturing process. Much polluttional material can be kept out of the streams and need not be handled in a treatment plant if it can be salvaged and re-used in the manufacturing process or recovered and utilized as a by-product.

In the electroplating industry, which is one of Michigan's major industries because of its relation to the manufacture of automobiles, many plants now recover the chromium compounds from their rinse waters, and re-use these in the plating process. Loss of chromium from electroplating solutions by drag-out on the plated parts is very large, because the solutions are concentrated and viscous and because the size and shape of many parts do not permit adequate draining in a conveyorized plating line. It is common practice to remove this adhering chrome liquor by a series of two to five rinse tanks. Frequently low-volume fresh water sprays are used to aid the rinsing. By utilization of the countercurrent flow principle, or by employment of standing or dip rinse tanks, the rinse water can be built up in concentration to a considerable

fraction of the strength of the main plating solution, and no foreign matter is introduced in the process. It is a relatively simple operation, therefore, to further concentrate the rinses by evaporation, so they can be returned to the plating bath. Large glass-lined vacuum evaporators are used for this purpose in a number of plants, and they salvage many pounds per day of chromic acid that would otherwise be lost to the sewer. No particular difficulties are encountered, other than the scheduling of evaporator cycles and the transportation of rinse waters and concentrated liquor. Missionary work may be necessary to persuade plating foremen that the recovered material is as good as purchased salt, but this problem is solved as soon as they realize the economic benefit to their department operations.

Another example of material salvage from electroplating wastes is the recovery of copper and nickel salts by ion exchange. Segregation of the individual rinses is of course necessary, but the operation is practical and often economical. Several such installations are in use in the Michigan automobile and automobile hardware plants. Generally the rinse overflows are pumped to holding tanks, and then through the ion exchange resins. Regeneration with sulfuric acid produces a solution of copper or nickel sulfate strong enough to be returned to the plating tanks.

Chromium can also be recovered from dilute wastes by ion exchange. However, the regenerated product is not suitable for return to the plating tank or chromate-treatment tank because foreign ions are inevitably present. Instead, consideration is generally given to salvaging the recovered chromium as barium chromate, a yellow pigment. I cannot report success in the marketing of this by-product, but it should have a sales value, and market studies are in progress. Several companies are stock-piling barium chromate in drums in hopes of a market when their supply is greater.

In the paper industry, an example of by-product utilization of waste is provided by the Otsego Falls Paper Mills in their roadbinder program. Semichemical pulp liquor from hardwood pulping is a serious stream pollution problem, even though it is only one-third as strong as the waste process liquor of the earlier sulfite process. Several by-product recovery schemes were studied by this company, the technique finally adopted involved utilization of the liquor on roads to stabilize the soil and keep down dust. Large quantities of the waste have been used during the summer months, when disposal to the streams is most objectionable. For best results on the roads, a concentration of 10 to 15 percent solids is necessary. The Otsego wastes contained only 4 to 5 percent solids, but in-plant modifications made it possible to raise the concentration to the desired point. This was accomplished by using less water in the cook and by more carefully controlling the operating temperatures and pressures. Application of waste liquor at the rate of one gallon per 13 square feet of road surface was immediately beneficial, and successive applications improved both the road surface and the deeper layers of sub-soil.

In 1954, the Otsego mill used 3.9 million gallons of waste as road binder. This amounted to 81 percent of the total waste liquor produced, or an 81 percent decrease in pollutorial material discharged.

In 1955, the amount was 3.3 million gallons, or 71 percent. The Munising Paper Company has conducted a similar operation, using waste calcium-base sulfite liquor.

Underground Disposal

The underground discharge of waste brines from petroleum production and chemical manufacture has been practiced for many years, not only in Michigan but in other states and in Canada as well. If the injection is deep enough, and if it penetrates a non-potable aquifer, no harm results from such disposal. No suitable treatment means exists for these high chloride wastes, and they must be discharged where they will not cause harm.

At the Dow Chemical Company, underground disposal is used not only for brines but also for certain strong organic wastes which are not amenable to the usual techniques of treatment. At the Upjohn Company, in Kalamazoo, concentrated organic wastes from pharmaceutical and antibiotics manufacture are treated by neutralization, precipitation, and settling prior to injection into two 1200-foot wells. Similar antibiotics wastes are disposed of into deep wells at Holland, Michigan, by Parke, Davis & Company.

At Bay City, Michigan, the Bay Refining Company is disposing of spent caustic wastes into an injection well. The Ford Motor Company, at its Rouge plant, is currently developing a deep well process for getting rid of phenol-bearing coke-oven wastes.

High pressures are sometimes necessary to force wastes into the underground formation at the rate necessary. Too high a pressure, however, may lead to fracture of the geologic formation; this could result in formation of fissures that would convey the wastes into potable water aquifers. In Michigan, it has generally been required that pressures not exceed 1000 to 1200 pounds per square inch at the well head. Acidity in the waste may help to open up porosity in the rock and so increase the absorptive capacity of the well. Upjohn has found that somewhat lower pumping pressures can be used if the acid wastes are not completely neutralized. Strongly acid wastes, on the other hand, are undesirable from a corrosion viewpoint.

Spray Irrigation

The disposal of organic wastes by spraying onto woodland, pasture, or crops has become increasingly widespread in the past few years. This practice started in the cannery and dairy industries, where it is still most popular, but it has been tried on other types of wastes as well. Several articles on spray irrigation have appeared in the journals and experimentation and trial installations are currently active.

I might report that Michigan State University has a current research project with a nearby cannery to investigate various types of trees for spray field cover. A forest soil has higher absorptive capacity than grass or crop land, and this research, in the Forestry Department, is aimed at comparing various species of fast-growing trees native to this area. The plantings are now three years old, which is too short

a period for conclusive results, but indications are certainly favorable.

The usual goal of a spray irrigation system is to maintain a continuous growth of vegetation under spray conditions. This may not be possible if the waste contains an appreciable concentration of inorganic salts, because the vegetable tissues are dehydrated by such treatment. At a recent Purdue Conference, the American Box Board Company of Filer City reported on disposal of neutral sulfite pulp wastes. All vegetation in the spray area was killed within a few days, however, an abundant growth of grass and weeds appeared the following Spring. Apparently the inorganic salts were leached from the soil during the Winter, and the organic matter remained on the ground where it served as fertilizer and soil conditioner. It was anticipated that in about three years the porous condition of the soil would be restored and the area would be ready for a further application of waste. This practice necessitates several spray fields, each in a different phase of a 3- or 4-year cycle, but the results reported have been fully satisfactory.

Flotation

The flotation operation is sometimes used to accelerate the separation of solids or oils that neither sink nor float with sufficient rapidity. By attaching small air bubbles to the individual particles, a strong buoyant force is created and the solid or oily matter rises quite promptly to the surface, where it is easily removed. The least expensive means of providing the necessary bubbles is by injection of compressed air through a porous diffuser or by mechanical agitation or beating. However, these techniques are not nearly as effective as the nucleation method, although they frequently suffice for wastes relatively easy to separate.

A better technique is to cause air bubbles to form or nucleate in direct contact with the foreign particles. This is accomplished by forcing the gas to come out of solution in the liquid, in the form of bubbles. New bubbles have a natural tendency to form at discontinuities like the surface of particles, and to adhere to such surfaces. Nucleation of gas bubbles is achieved either by applying vacuum to air-saturated waste, or by dissolving air under pressure in the waste and then releasing the pressure.

The flotation treatment of wastes is usually adaptable to solid particles without difficulty. Its most useful application, however, is in the treatment of oily wastes and emulsions, since these are often difficult to separate by conventional inexpensive means.

Several metal-finishing plants in Michigan and elsewhere are separating emulsified or "soluble" oil wastes by vacuum or pressure flotation. Addition of chemicals is usually necessary for pH adjustment or flocculation, but the dosage of chemicals is small. Alum and activated silica have been used. In some plants, preliminary separation without chemicals produces an oil product that can be recovered for use on roads or as fuel, and final treatment with chemicals yields an effluent that is clean enough for discharge together with a final sludge or "float" of no value. Attempts to operate oil flotation units without chemical agents, either in the metal industries or at petroleum processing plants,

have sometimes been successful, but generally not.

Neutralization

The disposal of steel mill pickle liquor has been a problem for many years, and a great number of schemes have been investigated to minimize the costs and difficulties of treatment. Let me describe to you briefly one such installation that has been completed within the past month. This installation employs a modification of the Cooper Process, developed by Jack E. Cooper, and has been placed in operation at the McLouth Steel Corporation, near Detroit.

The McLouth operations include the treatment of blast furnace gas wash water with acid pickle liquor, for mutual neutralization and the precipitation of iron. Natural alkalinity of the wash water is supplemented by lime slurry additions, as needed to complete the reactions. The dilution, however, is great enough that calcium sulfate is not precipitated, but remains in solution and is discarded. The reaction sludge is therefore a relatively pure ferric hydroxide, which can be dewatered and sintered for charging to the blast furnace.

In a parallel operation at the McLouth plant, rolling mill cooling water containing mill scale and dust is similarly treated with pickle liquor and lime. Without such treatment the dust particles would not settle, but this type of flocculation produces a clear effluent instead of the previous dark red waste.

Biological Treatment

Biological treatment methods for organic wastes have attracted much interest in recent years. Many strong wastes which were formerly thought to be beyond the capabilities of microorganisms to destroy have been found amenable to such treatment after all. The experiences of Dow Chemical Company and others with the biological oxidation of phenol wastes is well known. These compounds, usually considered to be bactericides, can nevertheless be attacked and broken down by bacteria specially acclimated to the particular type of waste. Activated sludge, trickling filters, and perhaps other types of biological treatment can be utilized.

To my knowledge, no full-scale cyanide destruction by biological means is being undertaken in Michigan, but I do know that such studies have been considered and that a large pilot plant has been operated at the Buick factory. We are conducting some small-scale laboratory studies in certain phases of this work in my own department, and a year ago I had the privilege of describing at Purdue the rather astonishing results achieved by the British Water Pollution Research Laboratory. Under proper conditions, it appears possible to utilize the cyanide group as the sole source of carbon for the growth of microorganisms.

Two-stage biological treatment will be used to provide a high degree of purification of combined industrial and municipal wastes in the new Frankenmuth plant which starts operation in about two weeks. The combined waste includes 1/4 m.g.d. from a large brewery and an equal volume from the Village of Frankenmuth. The village sewage, even without the

brewery, contains sufficient organic industrial wastes to give it a BOD of 350 ppm and a suspended solids content of 300 ppm. The brewery waste is of course several times stronger, and the combined flow will be 540,000 gallons per day, at 1250 ppm BOD and 530 ppm suspended solids. In order to provide the high degree of treatment necessary, two extra large trickling filters will be operated in series with primary, intermediate, and final settling tanks. A recycle ratio of 5 to 1 is planned for each filter. The digesters also are oversize, based on conventional municipal practice. Because of the two-stage biological oxidation and the liberally designed biological units, it is hoped to realize a 97% reduction in BOD and 95% in suspended solids. The plant is scheduled to begin operation about July 1st, and it will be interesting to observe its progress.

Conclusion

This has been a rather rambling sort of talk but, as I warned you at the beginning, I have attempted to discuss briefly some of the recent developments in industrial wastes control that interested me. I hope you have learned something new from these remarks, and that you conclude, with me, that the control of industry wastes is receiving active study and advancement.

TOTAL OXIDATION WASTE TREATMENT

By

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This theoretical design of a waste treatment unit assumes that chemical treatment is impractical or impossible, and that good housekeeping measures are in practice. Thus biological processes are the only possibility, and fundamentally they are: aerobic and anaerobic. The bacteria involved in biological waste treatment have the unique ability to operate in the presence of oxygen or in its absence, but as one would suppose they do not produce the same end-products.

When the bacteria are aerobic and operate in the presence of oxygen they convert the waste pollution into new cellular protein material. This is the basis of aerobic waste purification. To dissolve the oxygen necessary for this process can be quite costly. It must also be borne in mind that supplying a fraction of the needed oxygen will not produce a fractional purification, but will result in fundamentally stopping the aerobic process.

In the anaerobic system, where no oxygen exists, the bacteria will decompose the pollution and produce gases and liquids. In this case nothing need be supplied except continual mixing and a source of carbon dioxide. Carbon dioxide is as essential to the anaerobic process as oxygen is to the aerobic process. Fortunately, however, carbon dioxide is one of the gases produced in this system, so it only becomes necessary to recirculate the gas produced. The recirculation will also mix the contents and the desired decomposition will proceed rapidly and uniformly.

By either process 90% - 95% of the pollution can be removed. It then becomes the problem of the sanitary engineer to determine which is the most economical system for the waste in question. The aerobic system requires 4-24 hours detention time (with a large supply of oxygen) whereas the anaerobic system requires the same detention time with a lesser power cost. Without becoming involved in the detailed mathematics it is obvious that a high BOD value (10,000 ppm or more) could be most economically treated anaerobically. Waste with low BOD values (less than 2000 ppm) can best be handled by the aerobic process. However these arbitrarily selected values leave a large gap (2000 to 10,000) which requires a combination of the two processes to achieve the most economical cost to the industry.

In the aerobic process where total oxidation is used, oxygen must be dissolved equal to the 20-day BOD of the waste. When this is done no sludge is withdrawn from the system since there will be none to withdraw, because enough oxygen is being dissolved to satisfy the entire BOD. The equilibrium total weight of sludge in the system will be approximately three times the daily weight of the 20-day BOD. This equilibrium results from these two principles developed by Hoover, Porges, et al.: a) one pound 20-day BOD is transformed into 0.52 pounds of new activated sludge, and b) the activated sludge undergoes an oxidation loss equal to one percent per hour.

In the aerobic process, as the BOD value of the waste increases so does the necessary amount of oxygen required. Thus it will prove more economical to withdraw the excess portion of the sludge not needed for purification of the waste and subject it to anaerobic decomposition rather than to oxidize all of the sludge produced in the purification process. After anaerobic decomposition the liquid effluent can be returned to the influent of the aerobic system for disposal as a component of the influent waste. However, the amount of sludge withdrawn must be limited so as not to reduce the total weight in the aerobic system too low, otherwise there will be insufficient sludge present to purify the waste, which, after all, is the basic purpose of the design. To permit the continuous return of excess activated sludge to the anaerobic digester it will be necessary to pasteurize it to 135°F. so as to destroy its aerobic enzyme system.

Whether the process design employs total oxidation, oxidation and digestion, or digestion "polished-off" with oxidation there is still the problem of dissolving oxygen for the aerobic process involved. During the last 20 years quite a procession of aerating devices has been used for activated sludge processes. The gamut has ranged from variations of drilled holes in the air leader to cavitation-shear devices, and includes diffusers and mechanical agitators. Basically the fundamental theory of all of them is the renewing of the maximum area of air-exposed liquid surface per unit time. Therefore the most economical and simplest way of exposing liquid surface is the most desirable method of aeration.

Recently a new product was developed and manufactured by The Dow Chemical Company, and has the name of Dowpac HCS. The basic component is a specially corrugated thin plastic (styron) sheet. These sheets are cemented together to make a module which has ten square feet of cross section (39 in. x 39 in.) and is 21 inches in depth. Any number of these modules can be "stacked" in a suitable configuration for hydraulic dosing.

Dowpac has 25 sq. ft. of surface per cubic foot and 95% void space. By virtue of its corrugated pattern and surface continuity it has the ability to create a large amount of new liquid surface per foot of downward flow. Thus it is basically a good surface-film aerator.

To evaluate the efficiency of Dowpac as a mechanical aerator, columns of it were dosed with a cobalt-catalyzed sodium sulfite solution, and the sulfite content analyzed before and after passage through the column. The sulfite oxidized would be a measure of the magnitude of air-exposed surface produced. The sulfite oxidation data mean little until they are compared to the values for completely saturated water. Since the sulfite solution was never completely oxidized because of a high concentration present, (comparable to water saturation) the data show that enough new surface is created in passage through a 63 inch tower to dissolve ten times the oxygen saturation value of water. It was noted that at a flow of 4 g.p.m./sq. ft. the surface is completely wetted and at greater flow rates the surface film is increasing in thickness. Assuming five seconds flow-through time, the film thickness is 0.1 inch for 10 g.p.m./sq. ft. flow.

It is assumed that the sulfite solution flow rates greater than 4 g.p.m./sq. ft. cause no gain in surface renewal -- therefore the water flow could be increased to values of 40-50 g.p.m./sq. ft. and still exit from the column saturated with oxygen.

Thus by pumping 40 g.p.m. (for example) to a total head of 20 feet (to include friction losses) this will mean 7.2 KWH, at an overall efficiency of 50%, to dissolve four pounds of oxygen per day - or essentially two KWH per pound of oxygen per day.

Assume a totally aerobic system of waste treatment (with total sludge oxidation) is desired. Once the ultimate weight of BOD is known the area and volume of Dowpac can be calculated, as well as the pump capacity. The Dowpac is located over the oxidation tank and the waste passed over it.

If a typical activated sludge process is to be used, involving wasted sludge, then the daily weight of oxygen needed is:

$$W = 0.37V + F(0.63U)$$

Where W is the weight of oxygen to be dissolved, V is the ultimate weight of BOD per day, and F is the fraction of activated sludge returned to the aeration tank.

Thus it is possible to actually design a biological oxidation system in terms of BOD just as soundly as a structural beam can be designed. No longer is there need for such parameters as cubic feet of air per gallon and pounds of BOD per 1000 cu. ft. Further, Dowpac HCS has no maintenance problem, nor replacement problem, and there is no submerged equipment.

It is possible for organic food wastes to be completely decomposed without a sludge problem, and to produce an acceptable effluent at the minimum annual cost of capital investment and operating expense.

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BIO-OXIDATIVE TREATMENT OF DAIRY WASTES

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"Deoxygenating wastes consist of all wastes which react with the oxygen dissolved in the receiving body of water and deplete or tend to deplete the amount of oxygen available for normal aquatic life." So stated DeLaporte at the First Ontario Industrial Waste Conference (1). Such a waste originates in the dairy and milk processing industry. Aerobic treatment is generally used for the disposal of dairy wastes because these wastes have a low concentration of solids and a high oxygen demand. There is, however, a record of failure as well as of success with aerobic treatment, and the underlying reason for the failures has been the lack of basic information on the aerobic process.

This report to the Conference presents results of our laboratory investigations, and contains basic information on the conversion of dairy waste by aerating sludge and on the oxygen requirement during the process. Much of the information may be applicable to other waste. Details are available in various publications and have been summarized (12, 13, 14, 16).

Milk Waste

Milk losses are inevitable. Under good housekeeping, 1% is a low operating loss, although as much as 3% or more of the milk or its equivalent may be found in the waste. Thus a plant handling 150,000 pounds of milk daily will discharge a minimum of 1,500 pounds fluid milk containing 180 pounds milk solids. Wash and cooling waters dilute this loss so that the dairy waste contains only 0.1% solids giving a concentration of 1,000 parts per million (ppm). The biochemical oxygen demand (BOD) would be about 800 ppm, while the chemical oxygen demand (COD) is around 1,000 ppm (9). The daily pollution load from such a milk plant would equal that of a community of at least 430 people.

The soluble solids in dairy waste serve as an excellent nutrient for microbial growth as they contain about 53% lactose, 35% protein and necessary salts. Extreme precautions are necessary to avoid the obnoxious conditions so generally known. An understanding of the biochemistry of the treatment process would help produce desirable effluents.

Gross Changes During Aeration

The problem was approached as one of aerobic fermentation of a very dilute solution. A laboratory fermentor was used throughout these studies (7). The device allows excess agitation and aeration. Malodors were absent when a simulated waste made from skim milk was fed continuously at the rate of one liter per hour into 20 liters of aerating solution. Examination of the non-settled mixed effluent showed that about 40 to 50% of the COD had disappeared. More detailed analysis showed that all the protein (determined as nitrogen) of the added waste was now in

the cell or sludge solids. Further, 44 units of the original carbohydrate were completely gone while 9 units were used as cell substance. Of 88 units of organic matter in the waste, one-half had disappeared while one-half remained as cell substance. Similar results were observed when 20% of aerator capacity served as seed while waste was added so that the container filled in 4 hours. The seed contained about 500 ppm solids. After two hours there was a rapid decrease of total oxygen demanding material until by the sixth hour there was only about 50% of the amount present in the original waste (5). Removal of cells by centrifuge gave a solution with only about 10% of the original COD.

Oxygen Uptake

The changes that occur during aeration were determined in the Warburg apparatus by manometric measurements made at 30°C in buffered solutions containing sufficient nitrogen nutrient. A well-aerated sludge was used as inoculum. The rates of oxidation of skim milk, as well as of lactose and casein, the major components of skim milk, were high for the first six hours and then approached the rate of the unfed control (4). In each case between 32 and 40% of the total theoretical required amount of oxygen was used. The CO₂ formed in each vessel was equivalent to the O₂ removed. Further analysis showed that all soluble material had been removed. The fact that no other products were found in the solution suggested that aerobic treatment of dairy waste must occur thus:



Composition of sludge

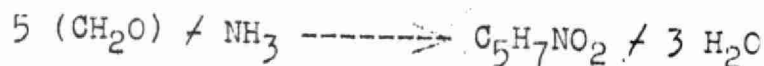
A more detailed consideration of this system required a chemical analysis of the cells as well as of the ingredients utilized by the cells. Dried sludge and casein were analyzed. The empirical formulas and mole weights were calculated and are shown in Table I. The ash content of sludge has been omitted but when this is taken into consideration the "mole" weight becomes 124 units instead of 113 as shown for C₅H₇NO₂. With the analytical data in the table, and information collected in the Warburg apparatus, certain bio-chemical relationships were established (8).

Removal of Lactose

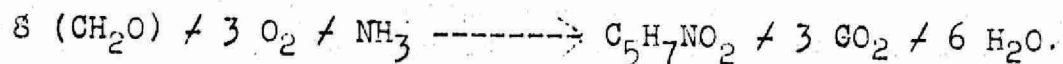
In the presence of a nitrogen source, lactose is readily removed from solution by aerated sludge. If complete oxidation of lactose occurred it could be represented by the well known equation showing that all carbon is oxidized, leaving none for the cells:



However, in order to obtain the 5 carbons in the cells, 5 sugar particles are needed:

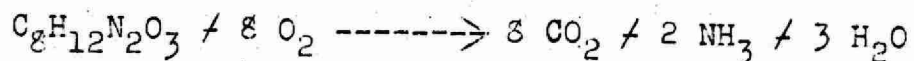


But the Warburg studies showed that only about 37.5% of the theoretical amount of oxygen was used; thus burning up three-eighths of available sugar to CO_2 and water, while the remainder was incorporated into cell substance. The utilization of sugar in the presence of NH_3 for cell synthesis must be therefore:

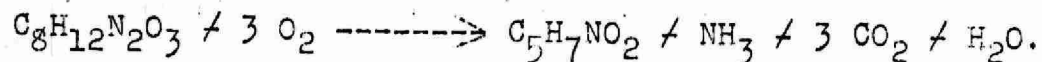


Removal of Protein

Similar reasoning showed how the casein, $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_3$, was used by sludge organisms. Theoretically, complete oxidation would be:

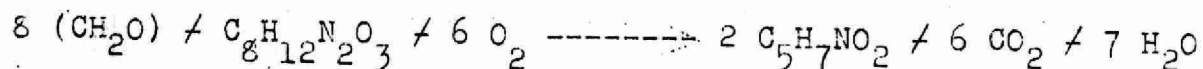


Manometric data again showed that only 3 of the carbons were completely oxidized. Thus casein was removed from solution for assimilation and oxidation in this manner:



Removal of Skim Milk Organics

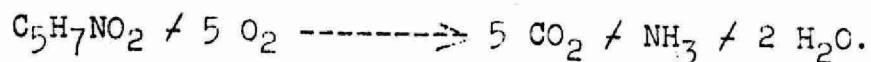
From the above, a mole of organic cell substance of 113 units may be formed from 240 units of sugar or 184 units of casein. Fortunately, this approximated the proportions of sugar and protein in skim milk. This permitted the addition of the two equations to give one equation for the assimilation of skim milk:



The nitrogen required for sugar assimilation is supplied by the protein. Therefore, 226 units of organic cell material may be produced from 424 units of organic milk solids, showing about 53% conversion to cells. The same value is obtained even when the ash and moisture content of the dried milk and of the sludge are taken into consideration. This approximates the values observed in many experiments.

Endogenous Respiration

Starving or unfed cells also have an oxygen demand and the Warburg studies showed that the organisms oxidized themselves thusly:



In order to completely oxidize 113 units of cells, there are required 160 units of oxygen. This endogenous respiration goes on very slowly. During the tests, 10 microliters of oxygen were used per mg of cell per hour. This equals 14.3 micrograms of oxygen, and from the equation of endogenous respiration, represented a destruction of 10.2 micrograms of cell substance, an amount equal to about 1% of the original weight of cells. Rates as high as 1.25% were observed in field trials. Lower rates may be anticipated as the more easily oxidized materials are used up.

Rate of Oxidation

Polarographic studies showed that an oxygen concentration of 0.35 to 0.5 ppm was necessary to maintain aerobic conditions (8). When 500 ppm sludge were treated with milk, the rate of oxidation was constant above a milk concentration of 100 ppm. The speed of milk oxidation was related to the cell concentration. If the cell concentration is doubled, milk oxidation should take half as long, but the same amount of oxygen would be required. After assimilation was completed, the rate of oxygen demand by endogenous respiration alone continued at one-tenth the rate required during assimilation.

Application of Data

From the data presented to this point, information is available on the amount of oxygen required for complete oxidation of a waste, the amount required during the rapid assimilation process, and the amount required for endogenous respiration. The rate at which oxygen is used by the sludge during assimilation and during endogenous respiration is also known. In addition, the amount of new solids produced can be calculated as well as the time required for such production.

Table II following shows calculations made for a single feeding of 100 lb of milk solids at 1,000 ppm concentration when acted upon by 500 ppm active sludge.

TABLE II

Calculations for Oxidation of 100 lb of Milk Solids (1,000 ppm Concentration) by 50 lb of Active Sludge (500 ppm concentration)

	<u>Assimilation Phase</u>	<u>Endogenous Respiration</u>	<u>Total</u>
Oxygen Required			
Per Cent	37.5	62.5	100.0
Pounds	45.3	76.1	121.4
Pounds per hour	7.5	0.75	
Time required (hours)	6		
New Cells produced (pounds)	50		
Cell solids oxidized (per cent per hour)		0.5-1.0	

Non-Accumulation of Sludge

A study of the above tabulation shows that conditions may be established favoring nonaccumulation of sludge. If it is assumed that 2,500 ppm sludge solids are in an aerator and endogenous respiration proceeds at 1% per hour, a total of 20% or 500 ppm will disappear in 24 hours. The addition of 1,000 ppm of skim milk will produce 500 ppm of new cells to replace the amount destroyed. In this way, it is theoretically possible to maintain a constant level of sludge while destroying waste. Kountz has successfully applied this principle to

industrial installations (10, 11).

Purification

Actually, the process is more than the simple assimilative oxidation of organic matter with subsequent oxidation of the cells by their own endogenous respiration. The rate of purification or removal of waste from solution is much greater than the rate of oxidation, as shown so well by Gellman and Heukelekian (3). They found the average rate of purification for seven industrial wastes to be six times the rate of oxidation. Our studies showed that when 1,000 ppm simulated milk waste were added to 1,000 ppm sludge in a single dose, purification rates were ten or more times greater than oxidation rates (6). In 30 minutes, one-half of the oxygen demanding substances was removed from the waste. According to the above equations, the expectation would be that the removal of nutrients would be eight-thirds or 2.67 times the rate of oxidation. Gellman and Heukelekian obtained such values for some wastes, but wider ratios were obtained with higher carbohydrate-type wastes. Since oxidation does not occur immediately, material is apparently accumulated for subsequent oxidation.

Storage and Oxidation

Further study with dairy waste showed that purification consists of several interrelated processes: removal from solution, synthesis, storage, and oxidation (15). A glycogen-like substance was the major storage product and was readily oxidized. It was estimated that during purification an active aerated sludge may store as much as 50% of its own weight. One would then anticipate that rapid and complete purification could be accomplished in about 20 to 30 minutes if 1,000 ppm of soluble organic substances were mixed with 3,000 ppm well aerated, starved sludge. The loaded sludge could be removed leaving a clear effluent. The concentrated sludge may be aerated to burn the stored material. The starved cells may be reused for seed or a portion of the loaded sludge may be disposed of by other means. Eckenfelder and associates have applied this process of purification and aeration of sludge slurry to various organic wastes (2).

Summary

Laboratory studies on dairy wastes have made available basic information of value to sanitary engineers. Specifically, each pound of oxygen demand requires a pound of oxygen for complete combustion. The high rate of oxygen utilization during assimilative growth must be satisfied to prevent obnoxious conditions. This phase of assimilation requires at least 37.5% of the total oxygen demand within a relatively short period depending upon the concentration of the sludge and of the solids. Oxygen is utilized at a much slower rate during endogenous respiration, and air flow may then be reduced about ten times. A significant amount of sludge is oxidized during the first 24 hours and may amount to as much as 20% of the sludge weight.

Equations of assimilation and endogenous respiration showing these changes have been developed and detailed data are presented.

The biological treatment is a complex process of water purification involving the multifold activities of microorganisms. Waste removal is a combination of cell synthesis, conversion for temporary storage, and oxidation. Application of basic information on synthesis, storage, and oxidation should be of prime consideration in designing biochemical treatment plants for waste disposal.

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TABLE I

Analytical and Empirical Composition of Milk
Ingredients and Sludge

Composition in %	Lactose	Casein	Sludge
Carbon	39.98	52.85	42.26
Hydrogen	6.72	6.48	5.69
Nitrogen	0	15.12	11.27
Oxygen	53.30	24.76	27.00
Ratio of Atoms = % /atomic weight			
Carbon	3.33	4.40	3.94
Hydrogen	6.71	6.43	5.65
Nitrogen	0	1.08	0.81
Oxygen	3.33	1.55	1.69
Formula:	$C_{12}H_{24}O_{12}$	$C_8H_{12}N_2O_3$	$C_5H_7NO_2$
Mole Weight	360	184	113

PRINCIPLES OF AERATION AS APPLIED TO WASTE TREATMENT

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Aeration may be broadly defined as an interphase mass transfer process. A summary of the transfer mechanism is presented. Detailed discussions of the mechanism can be found in the cited references (1 - 6).

Theory

Mass transfer by diffusion occurs between two phases when a driving force is created by a departure from equilibrium. This driving force is a partial pressure gradient in the gas phase and a concentration gradient in the liquid phase.

In aeration processes mass transfer by diffusion occurs from gas to liquid (absorption) or from liquid to gas (stripping) until a dynamic equilibrium is established. Mass transfer occurs through laminar films at the gas and liquid interfaces and through the turbulent body of fluid such that molecular and eddy diffusion processes will exist in series. Each of these diffusional resistances will vary with fluid turbulence.

Present methods of calculation consider the entire transfer resistance to exist in the laminar boundary layer across which molecular diffusion occurs so that it is necessary to interpret the nature of these boundary layers.

The boundary layers may be considered as hypothetical interfacial films of gas and liquid which provide a barrier to diffusion. These films exist only in a statistical sense and may be considered as a diffuse layer of varying concentration from saturation at the interface to the bulk fluid concentration some distance from the interface. This distance depends upon fluid characteristics.

It is assumed that a dynamic equilibrium is established at the interface (e.g. for each molecule which diffuses from gas to liquid one counter diffuses from liquid to gas). Since no concentration build-up will occur at the interface itself, the diffusional resistances may be considered in series and the controlling rate will be that which offers the greatest resistance to diffusion. It can be established from theoretical considerations that in the absorption or stripping of slightly soluble gases, such as oxygen and carbon dioxide in water, the greatest resistance occurs in the liquid film while in the absorption or stripping of highly soluble vapors, such as acetone, the gas film resistance will control.

Several concepts have been developed to define the mass transfer mechanism. Whitman (1) proposed a two-film theory which may be defined by the equation:

$$\frac{dw}{dt} = k_g A (P_g - P_1) = k_L A (C_s - C_L) \quad (1)$$

The liquid film coefficient k_L is defined as the liquid diffusivity divided by a hypothetical film thickness x .

Dankwertz (6) defined the liquid film coefficient as the square root of the product of the diffusivity and the rate of surface renewal ($k_L = \sqrt{D r}$). The rate of surface renewal, r , may be considered as the frequency with which fluid with a solute concentration C_L is replacing fluid from the interface with a concentration C_s . This establishes a layer with an equilibrium concentration C_s at the interface and a concentration C_L in the bulk of solution. The thickness of this layer (analogous to film thickness in two film theory) will vary with fluid turbulence. It becomes apparent that increasing the frequency of interfacial renewal must decrease the hypothetical film thickness thereby decreasing the distance over which laminar diffusion must occur. This results in an increase in k_L .

Considering the liquid film resistance Equation (1) may be re-expressed in concentration units.

$$1/V \, dw/dt = dc/dt = k_L a (C_s - C_L) \quad (2)$$

$$\text{where } k_L a = k_L A/V \quad (3)$$

$k_L a$ is a function of the variables previously defined and can be related to an exponential function of the Reynolds and Schmidt numbers through dimensional analysis. The Reynolds number accounts for the influence of turbulence and the Schmidt number the influence of diffusivity. High values of $k_L a$ are indicative of efficient aeration.

The gas film coefficient $k_g a$ can be correlated in an analogous manner. These mechanisms are illustrated in Figures 1 and 2.

Aeration Applications

Since the equilibrium concentration of carbon dioxide in water is only 0.5 ppm at 20°C, concentrations in excess of this can be removed by aeration. The mass transfer is assumed to be liquid film controlled. In unpublished studies, Riddick (7) obtained 95% CO₂ removal after 15 minutes aeration from an initial concentration of 90 ppm. $k_L a$ was of the order of 20/hr with an air flow of 120/cc/min/liter.

Cyanide in acidic solution will be removed by aeration. Cooper (8) showed 88% removal of HCN from an initial concentration of 610 ppm after 100 hours aeration at an air flow of 68 cc/min/liter. The transfer coefficient was of the order of 0.02/hr.

Removal of dilute aqueous solutions of volatile solvents by aeration is gas film controlled. In laboratory studies the transfer coefficients obtained ranged from 0.016/hr for alcohol at 21°C and an air flow of 275 cc/min/liter to 1.70/hr for methylethyl ketone at 70°C and 400 cc/min/liter. (9)

FIGURE 1

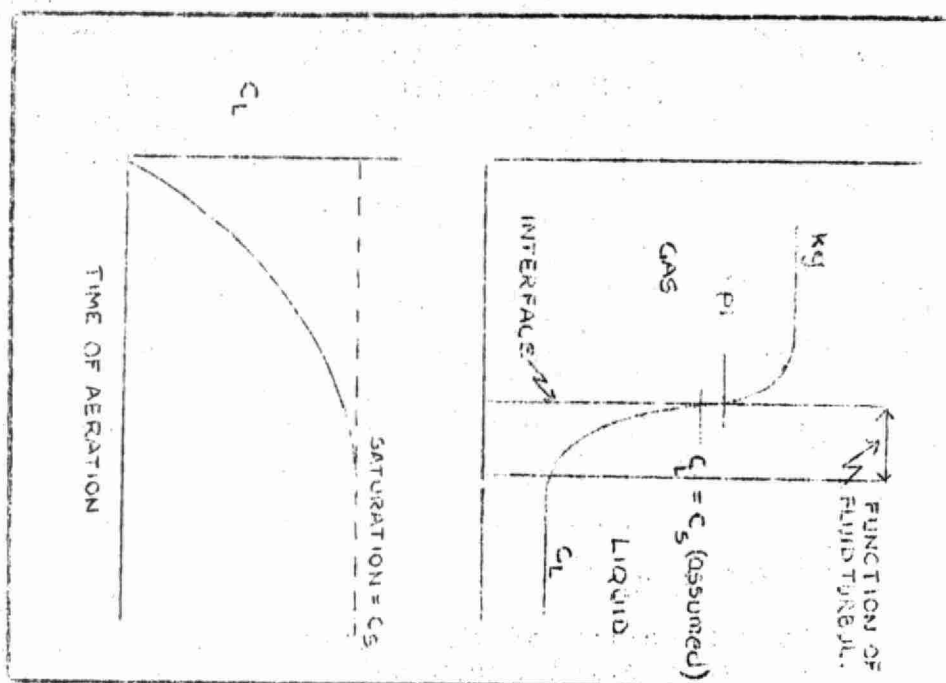
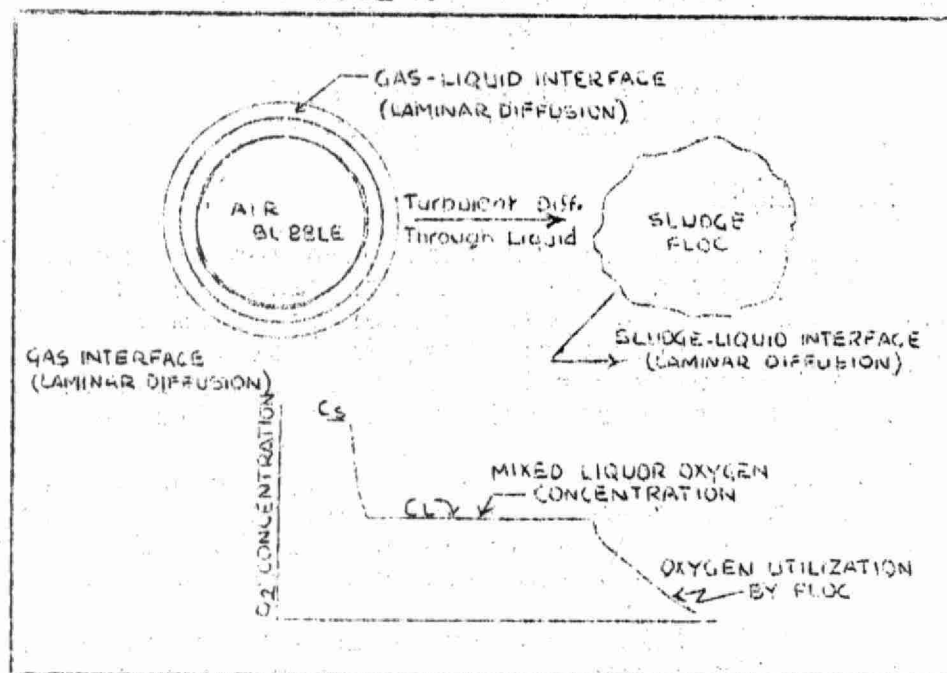


FIGURE 2



OXYGEN TRANSFER MECHANISM

In biooxidation processes oxygen dissolved in the liquid further diffuses into the microbial cell where it is consumed in the respiration process. To account for this oxygen consumption Equation (2) must be modified:

$$dc/dt = k_L a (C_s - C_L) - k_r S a \quad (4)$$

Normal biological waste treatment plant operation approaches a steady state condition where the dissolved oxygen level in the aeration tanks is maintained substantially constant and Equation (4) may be expressed:

$$k_L a (C_s - C_L) = k_r S a \quad (5)$$

The Mass Transfer Coefficient $k_L a$

$k_L a$ is a function of bubble size and interfacial area, volume of liquid under aeration, time of contact of air with liquid, tank depth, agitation intensity and other physical and chemical variables characteristic of the system. These various factors will be discussed particularly as they relate to the design and operation of waste treatment processes.

$k_L a$ can be expected to increase with increasing air rate due to an increase in available interfacial area and in increase in fluid turbulence. The bubble size released by a diffuser will vary from 1 - 100 times the orifice diameter. Bubble diameters for conventional diffusion equipment will vary from 1.5 - 4.0 mm. The bubble is formed in less than 0.1 seconds and steady state conditions exist 0.01 seconds after the film formation. Air flow rate for a diffusion device under specific operating conditions can be related to $k_L a$ by the exponential function.

$$k_L a = C G_s^n \quad (6)$$

Hixon and Gaden (10) found a range in the exponent n of 0.33 - 0.82 over a wide range of bubble fineness and dispersion. The fine bubble dispersers produced higher transfer at low air rates (larger interfacial area) while higher transfer was obtained from the large bubble spargers at high air rates (increased turbulence). The gas rate exponent n for most commercial diffusion devices varies from 0.6 - 0.9. (11)

As the liquid head above a diffusion unit is increased the total percentage of absorption will increase and the transfer coefficient $k_L a$ will decrease. Absorption occurs during bubble formation during the rise of the bubble through the liquid and by the bursting of the bubble at the surface and surface turbulence. The first and third absorption phases may be considered as end effects and will be substantially independent of liquid depth. Overall transfer during bubble rise has been found to vary from 6 - 12 percent per foot of rise through the tank liquid. (12) Exponential relationships between absorption and tank depth have been developed by several investigators. (13) (14) Considering end effects absorption can be related to depth

through the correlation:

$$k_{La}/G_s n = C (C^1/d - 1) \quad (7)$$

While an increase in temperature tends to lower the overall absorption rate due to decreased oxygen solubility, k_{La} will increase with temperature due to an increase in the diffusivity of oxygen in water and to an increasing turbulence due to a reducing viscosity. (15) This relationship may be expressed by a modified Stokes - Einstein Equation:

$$\frac{k_{La}(T_1)}{k_{La}(T_2)} = \sqrt{\frac{T_1}{T_2} \cdot \frac{U_2}{U_1}} \quad (8)$$

Where T is absolute temperature and U is viscosity, k_{La} at 10°C will be 86 percent and at 30°C , 114 percent of the rate at 20°C .

Other transfer rate-temperature relationships have been derived by Haslam (16), Pasveer (17), Velz (18), King (13) and Bartholomew (20).

The gas film coefficient $k_g a$ is less influenced by temperature. The gas film coefficient will vary as the square root of the absolute temperature. (21)

The oxygen absorption capacity of sewage and industrial wastes will vary from that in pure water due to changes in surface tension and viscosity. Reduction of surface tension reduces k_L due to the creation of a high diffusion barrier at the interface. (20) Bubble size decreases with decreasing surface tension, thereby increasing the interfacial area for transfer per unit volume. Very small quantities of added surface active agent can change the effective bubble size as much as 100 times. (22) Visual observations on the aeration of peptone and syndets showed a change in bubble size from coarse in water to fine in the presence of the added constituent. Reduction in bubble size decreased the rate of surface renewal due to a slower rate of bubble rise and a reduced shear at the bubble boundary. (23) In the presence of surface active agents, increased diffusional resistance and lower surface renewal rate exert a greater influence on k_{La} than the increase in interfacial area.

In order to compare the transfer rate in wastes to that in water, a coefficient α is defined as the ratio of k_{La} in waste to that in water under specified operating conditions. α will decrease from 1.0 in water to 0.5 in the presence of 25 ppm of peptone. Peptone concentrations of 1000 ppm reduce α . Lynch and Sawyer (25) found a variation in α of 0.35 - 1.10 with 50 ppm of various anionic and nonionic commercial detergents. Addition of a silicone antifoam to water reduced the absorption rate by 35 percent. Kehr (26) showed a reduction in k_{La} in stream reaeration in the presence of oils, soaps and organic acids and raw and treated sewage.

Extensive studies by King (13) showed α to vary from 0.26 - 0.46 for fresh sewage and from 0.16 - 0.19 for septic sewage.

67.

α was found to be 0.6, 0.7 and 1.4 for chipboard repulping wastes, Kraft Mill mixed wastes and semichemical paper machine wastes respectively.

Biooxidation which alters the physical and chemical properties of waste mixtures modifies α to a value approaching that of water. In activated sludge treatment of domestic sewage α increased from 0.72 to 0.90 after 4 hours of aeration.

Treatment of Kraft Mill waste increased α from 0.45 to 0.79 after 3 hours of aeration with activated sludge.

High mixed liquor solids concentration in activated sludge processes reduce $k_L a$ by altering the physical properties of the aerating medium. In the presence of 10,000 ppm sludge solids absorption was only 1/5 that in pure waste. (27)

Measurement of $k_L a$

Overall transfer coefficients can be determined by one of several procedures. These include the sulfite oxidation test, non-steady state transfer in deaerated water and steady and non-steady state transfer in sludge-liquid systems.

Sulfite Oxidation (28) (29) (30)

In the presence of copper or cobalt salts which act as catalysts, the reaction between sulfite ion and oxygen or air proceeds rapidly and irreversibly to completion in aqueous solution. The rate of the chemical reaction is considerably more rapid than the absorption of oxygen. The rate is independent of sulfite ion concentration above approximately 2000 ppm.

Water or waste is prepared 0.2N in sulfite ion and 10^{-3} molar in cupric ion (Cobalt may be substituted for copper). Air is applied at predetermined rates and samples withdrawn at periodic time intervals (3 - 20 minutes) depending on the air flow and absorption rate. The rate of oxygen absorption is measured by determining the difference between the unoxidized sulfite ion concentration before and after aeration.

An aliquot sample depending on the unoxidized sulfite ion concentration is pipetted into each of two flasks containing 50 ml. of 0.1 iodine solution. During the transfer the tip of the pipette should be held close to the surface of the iodine solution to avoid aeration. The unoxidized sulfite ion is then determined by an iodimetric procedure of back titration with standard thiosulfate solution to a starch indicator endpoint. To minimize sulfite oxidation during transfer the pipettes should be rinsed with distilled water and flushed with nitrogen from 2 - 3 minutes prior to sampling.

Results are expressed as ppm O_2 absorbed per hour which is $k_L a C_s$.

Non-Steady State Aeration

Overall transfer coefficients may be determined by non-steady state aeration under standard conditions, in which the transfer rate is computed from the change in oxygen concentration of the sample under aeration.

The dissolved oxygen present in the sample is stripped with a nitrogen purge. Air is then diffused into the sample at a specified rate and the dissolved oxygen concentration measured at selected time intervals until the sample is approximately 90 percent saturated.

The transfer plot may be obtained over a 12 minute aeration period, applying metered air to a liter graduate of sample through an aloxite diffuser stone. The dissolved oxygen content may be measured either with a polarograph or by chemical methods.

The none-steady state absorption of oxygen follows the exponential function shown in Equation (1). $k_L a$ is computed from the slope of a plot of the saturation deficit ($C_s - C_L$) vs. time of aeration.

Biological Oxidation Systems - Steady and Non-Steady State

In many cases it is desirable to evaluate $k_L a$ under operating conditions in bio-oxidation systems. If steady state conditions are maintained $k_L a$ can be directly computed from Equation 5. $k_L a$ may also be determined employing a non-steady state procedure.

The air is turned off and the dissolved oxygen level permitted to approach zero through microbial respiration. Air is then admitted at the desired rate and samples withdrawn at 1 minute intervals for dissolved oxygen measurement. Sampling is continued until a steady state condition is approached. The oxygen utilization rate and saturation value are determined as previously described. $k_L a$ is determined by a procedure of successive approximation according to Equation 4.

Oxygen Transfer Efficiency

Oxygen transfer efficiency is defined as the fraction of oxygen absorbed of the total applied to a system.

$$\text{o/o Efficiency} = \frac{\text{weight of oxygen absorbed per unit time}}{\text{weight of oxygen supplied per unit time}} \times 100 = \frac{R_d}{G_s} \times 100$$

in which

$$R_d = k_L a (C_s - C_L) \cdot 8.34 \cdot \text{mg of tank capacity} =$$

$$\text{and } r_r \cdot 8.34 \cdot \text{mg of tank capacity} = \text{lbs } O_2/\text{hr}$$

$$G_s = \text{air flow (cfh)} \cdot \text{density } \left(\frac{\text{lbs air}}{\text{cu ft}} \right) \cdot 0.232 \left(\frac{\text{lbs } O_2}{\text{lb air}} \right)$$

the air density is related to the temperature and pressure of the air

$$\rho = 0.0808 \frac{(P_a)(492)}{(14.7)(T_f)}$$

Oxygen Saturation

Oxygen is a sparingly soluble gas in pure water whose equilibrium relationship is defined by Henry's Law. While the solubility is almost independent of the total pressure and the presence of other gases, it is directly proportional to the partial pressure of oxygen in the gas phase.

The factors of importance which influence the saturation concentration of oxygen are (a) partial pressure, (b) temperature and (c) the presence of dissolved and other solids.

The partial pressure is influenced by the increased pressure of the entering air which is usually released at a 12 - 15 foot depth in waste oxidation practice. Oxygen is also absorbed by the rising air bubbles reducing the oxygen concentration in the gas phase. These effects may be approximately computed from Equation (9). (Vapor pressure effects and variable saturation characteristics for surface aeration and bubble formation are neglected.)

$$C_s = f C^* \left\{ \frac{P_b}{29.4} \right\} / \left\{ \frac{O_t}{42} \right\} \quad (9)$$

Temperature effects have been well defined in the literature (31). Wastes of variable composition will alter the equilibrium relationships. For example, oxygen saturation in sewage is approximately 95 percent that of pure water (32). Various waste streams from pulp and paper manufacture have shown variations of 85 - 95 percent of pure water saturation. Saturation characteristics may be measured polarographically or chemically on well aerated waste samples.

Oxygen Utilization

Oxygen utilization may be defined as the weight of oxygen consumed per unit weight of biological sludge per unit of time. It is usually expressed as mg O₂/hr/gm sludge. The total oxygen uptake rate in a system will be the product of the unit rate and the sludge concentration carried in the aeration tanks.

The uptake rate characteristics will vary as the sludge passes through various growth stages. The rate can be generally considered in two phases; active respiration which occurs in the presence of nutrients and is characteristic of a growing sludge and endogenous respiration which is the auto-oxidation of cellular tissue. The endogenous respiration rate is 5 - 10 percent of the active respiration rate. Quantitative relationships may be found in the cited references (33) (34) (35).

In the long rectangular aeration tanks used in conventional activated sludge practice, the sludge-liquid mixture is rolled down the tank length with a spiral motion imparted by the air and as the BOD in the influent waste undergoes oxidation and synthesis, the oxygen utilization rate decreases approaching the endogenous level. This level is approached toward the end of the aeration basins.

A variable utilization rate will usually not be found when square or circular tanks are employed. The homogenizing effect of the agitation and aeration will tend to equalize the utilization rate at the mean level.

In order to take economic advantage of this decreasing utilization rate through the aeration tanks, tapered aeration can be employed. $K_L a$ can be adjusted to meet the necessary demand by the number of individual aeration assemblies reducing along the tank length or the air rate can be regulated at each point in the aerator by appropriate valving. In deriving a tapered aeration design the variation in $K_L a$ with oxidation must be considered. The value of $K_L a$ relative to water, α , will increase the oxidation.

Aeration Equipment

There are three basic types of aeration devices commercially available:

- (a) Porous media type orifice diffusion units. Common types are (1). Plates or tubes constructed of silicon dioxide or aluminum oxide grains held in a porous mass with a ceramic binder and (2) saran or nylon wrapped tubes or bags. These units may be permanently placed in the bottom of an aeration tank or suspended from flexible joints along the sidewall of a tank. When air is diffused through these units, a helical or screw motion is imparted to the sludge-liquid mixture.
- (b) Units employing a mechanical or air shear such as the impingement or jet aerator.
- (c) Mechanical aerators which entrain atmospheric oxygen into the sludge by surface agitation or disperse compressed air by a shearing and pumping action employing a rotating turbine or agitator. In the latter unit, air is discharged from large diameter orifice in the form of a pipe or sparge ring beneath the agitator and is broken up by the shearing action of the high speed rotating blades of the agitator moving through the liquid. As the speed of the impellor is increased, the bubble size is decreased and the holdup increased thus increasing the total interfacial area. Bubble diameter has been shown to vary inversely as the three halves power of the peripheral speed (36). As the bubbles rise away from the impellor, the mean diameter increases due to coalescence. The relative effect of liquid pumping and air shear depends upon the size of the agitator with respect to the tank. For systems of low oxygen utilization rate, oxygen may be supplied by air self induced from the negative head produced by the rotor. This eliminates the necessity for external blowers or compressors.

Standard porous diffuser units are designed to deliver 4 - 8 cfm per unit. The absorption efficiency depends on the size of air bubbles released. This in turn depends on the type and porosity of diffuser unit. King (13) has shown the bubble diameter to vary from 2.5 - 3.8 mm for 40 - 80 porosity tubes or plates. Using the 60 porosity tube as a base, a 40 porosity unit will be 115 percent as efficient and an 80 porosity unit 85 percent as efficient.

In order to maintain adequate circulating velocities, a minimum air flow of 3 cfm per lineal foot of tank must be maintained. The minimum spacing of units is 6 inches and the maximum spacing 2 feet.

The maximum width to depth ratio to insure adequate circulation is 2:1. Suspended diffusion units are generally placed 2 feet above the floor of the aeration tank. Diffuser plates are usually placed along one side of the bottom of an aeration tank designed to cover 5 - 10 percent of the tank area. High maintenance costs may be encountered in some waste applications due to orifice clogging, etc.

The jet aerator pumps liquid from the aeration tanks through a piping manifold. The unit aspirates and disperses atmospheric air or air from a blower within the ejectors capacity. A wide range of oxygen absorption can be obtained depending upon the selection of operating variables. Studies by Kountz (12) showed that the rate of dissolved oxygen supplied is a function of the nozzle stream surface velocity as is also the air volume aspirated. For various units 0.66 - 1.0 lbs O_2 /hour can be transferred at liquid pumping rates of 34 - 44 gpm. These values can be increased by about 50% by supplying additional air with a blower. 18.3 - 20 percent absorption has been reported by Hauer in sulfite oxidation (37). Power consumption is a consideration since the liquid is circulated at 25 - 30 psi pressure. Orifice clogging problems may result in certain applications.

The impingement aerator employs a water stream air lifted from the aeration tanks as a shearing device for air bubbles discharged from a large orifice. The control variables are the impingement liquor flow, air flow and the location of the water nozzle relative to the air orifice. The units are usually installed in headers up to 40 feet in length with impinger bowls and water nozzles saddle mounted to the air and water headers at from 15 - 24 inch centers. Each unit is designed to diffuse 4 - 16 cfm of air with an impinger liquor flow of 15 - 20 gpm. The bubble size released depends on the quantity of impingement liquor flow delivered by the circulating air lift pump. Absorption increases linearly with impingement liquor flow over the range normally employed in practice. The power required for pumping impingement liquor is 8 - 15 percent of the total power for aeration. Over the normal operating range transfer efficiencies of 10 - 12 percent can be expected based on sulfite oxidation tests (38). The necessity for air filters is usually eliminated.

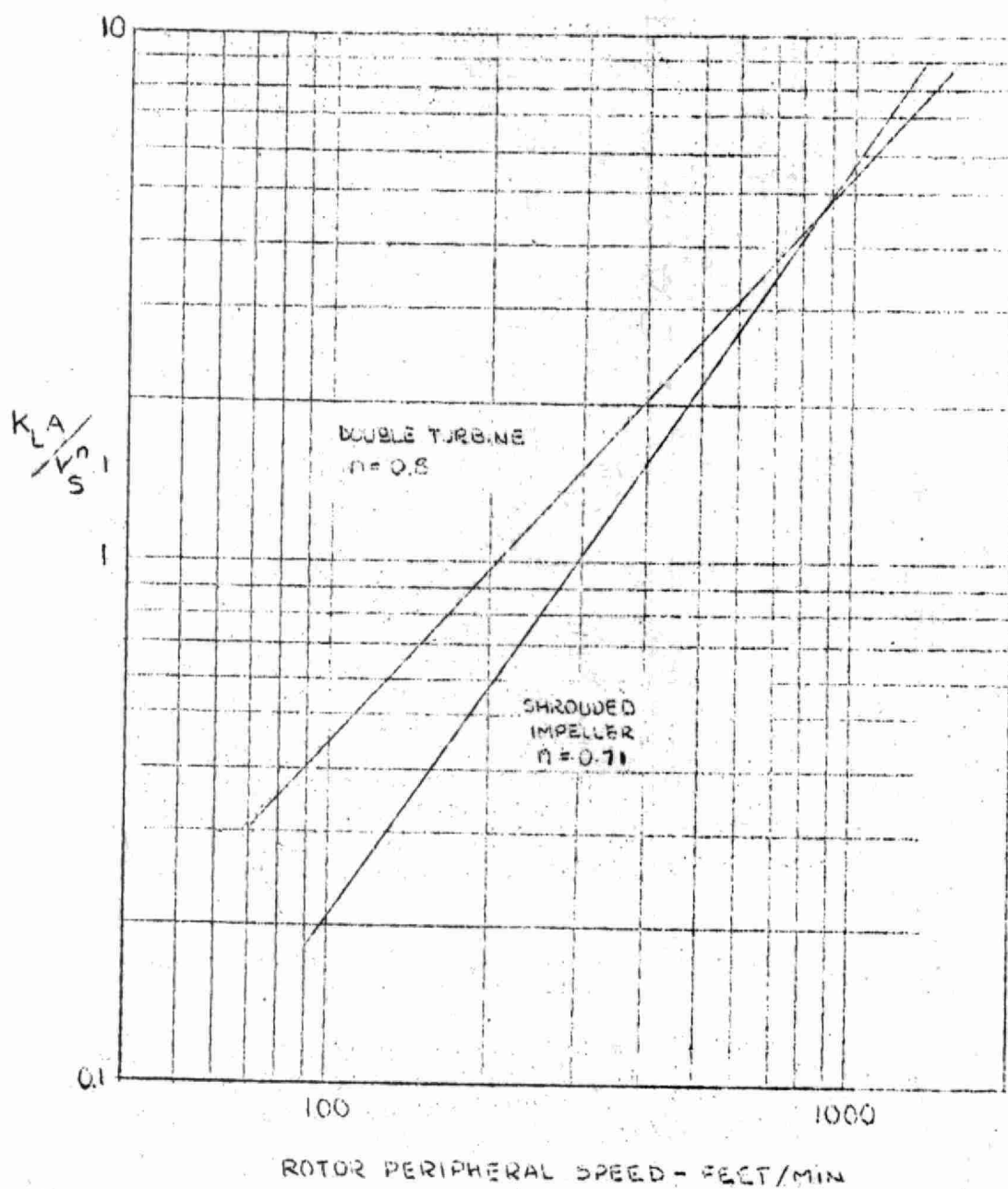
Other diffusion units operating under similar principles include the Colaflex diffuser and the Diffusair assembly.

The turbine aerator finds principle application in the treatment of high BOD industrial wastes. While the absorption limit of most diffused aeration units is 150 lbs O_2 /day/1000 cu ft mechanical aerators can disperse as much as 600 # O_2 /day/1000 cu ft.

Oxygen absorption in the turbine aerator will be a function of the air flow rate and the power input to the rotating agitator. A general relationship can be expressed by the formula

$$K_L a \quad V_s^x H P^y \quad (10)$$

Data obtained on sewage oxidation in a three foot square tank with a three foot liquid depth and four inch diameter impellers is shown in accompanying figure 3. The exponents x and y in Equation 10 have



OXYGEN TRANSFER CHARACTERISTICS OF TURBINE AERATORS
IN SEWAGE OXIDATION AT 3 FOOT LIQUID DEPTH

FIGURE 3

been evaluated for several systems and have been found to vary from 0.67 to 0.83 and 0.8 to 1.54 respectively.

Other formulations have shown the oxygen transfer efficiency to be directly proportional to the three halves power of the peripheral velocity and inversely proportional to the square root of the ratio of the total air flow to the peripheral area (39).

Power Requirements

When the concentration of dissolved oxygen in solution exceeds 0.2 - 0.5 ppm, the rate of microbial respiration is independent of oxygen concentration. In addition to maintaining oxygen levels in excess of the critical level, power must be supplied for mixing. Sludge cells tend to clump, hence to decrease the quantity of oxygen which can be transferred to them. The rate of oxygen diffusion into the sludge is related to floc size, diffusivity, oxygen utilization rate and the oxygen concentration level in the liquid. Increased power levels will disperse the sludge and increase the transfer rate.

Assuming a spherical floc, the minimum radius to insure oxygen throughout the floc may be defined:

$$r = \sqrt{\frac{3D(C_L - C_M)}{k_r Q}} \quad (11)$$

The specific gravity of the sludge Q will usually vary from 1.018 - 1.20 (40). C_L is the oxygen concentration at the floc - liquid interface and C_M the concentration in the floc center.

The power level is limited, however, by the necessity to avoid excessive floc shearing for subsequent solid-liquid separation.

Aeration Design

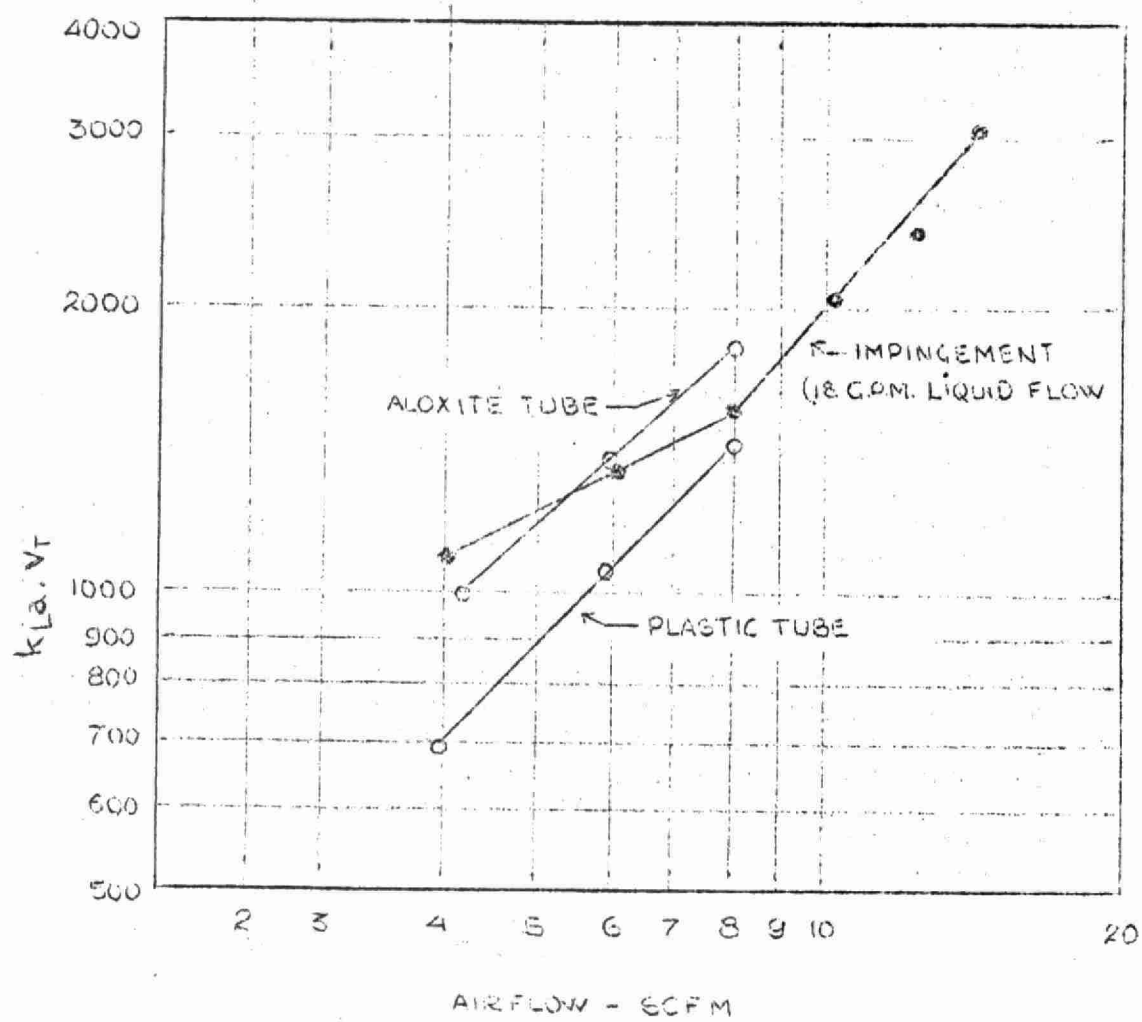
For practical design considerations it may be assumed that the quantity of oxygen transferred per unit time by the air diffusion unit within the critical area of air dispersion is a function of depth, temperature, gas flow and waste characteristics. The transfer characteristics of diffusion units at specified depths may be related by the absorption number $\frac{K_L a \cdot V_T}{G_s n}$

Equation 12 provides a convenient relationship for design at a specific temperature and depth

$$K_L a = C G_s^n \cdot 1/V_T \quad (12)$$

Data for various diffusion units derived from sulfite oxidation at 20°C is shown in accompanying figure 4.

In diffused aeration systems $K_L a$ may be varied by - (a) unit spacing selection; (b) diffuser permeability or other variable selector



DIFFUSED AERATION PERFORMANCE CURVES

FIGURE 4

which defines bubble size; (c) air flow. In turbine aerators $K_L a$ may be varied by either the impellor speed or the air flow.

A suggested design procedure for aeration systems in biological oxidation processes is outlined below:

1. Compute the oxygen saturation characteristics, C_s , at process operating temperatures and pressure for the particular waste to be treated according to Equation 1.
2. The minimum operating dissolved oxygen level should be maintained between 0.5 and 1.0 ppm to insure aerobic action.
3. The unit oxygen uptake rate for various BOD removal levels can be estimated from an experimental plot.
4. The oxygen demand distribution will be a function of time of aeration. This may be obtained by a laboratory study. The actual demand distribution in the aeration tanks will depend on the hydraulic characteristics of the particular tanks as designed.
5. $K_L a$ for each section of the system can be computed from Equation 5.
6. Aerator performance in sulfite solution at 20°C and 13 foot submergence depth can be obtained from Figure 4 or from data similarly derived. The operating $k_L a$ derived from Equation 5 must be corrected for temperature if the operating temperature deviates from 20°C and for the oxygen transfer coefficient, α , of the specific waste.
7. From Figure 4 (or a similar plot) the unit air flow - volume factor to transfer the required oxygen is selected.
8. After selecting a tank width and an air flow/unit, the unit spacing is computed.
9. This should establish the design for the most severe operating conditions. Under less severe conditions (winter operation, lower BOD loadings, etc.), the reduced required air flow can be computed in a similar manner.

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EXAMPLE(a) Oxygen Uptake Rate Calculation

The average oxygen uptake rate in an aeration tank is 36.8 ppm/hr. The average uptake in each quarter section of the tank is:

<u>Tank Length - o/o</u>	<u>Ratio to Mean</u>	<u>Uptake rate; ppm/hr</u>
0-25	1.3	$1.3 \cdot 36.8 = 47.9$
25-50	1.0	$1.0 \cdot 36.8 = 36.8$
50-75	0.8	$0.8 \cdot 36.8 = 29.5$
75-100	0.7	$0.7 \cdot 36.8 = 25.8$

(b) Calculation of Required α

$$\begin{aligned} \alpha & \text{ for raw waste} = 0.60 \\ \alpha & \text{ for effluent} = 0.90 \end{aligned}$$

If the recycle is 30 percent the average α at the influent end of the tank is

$$0.7 \cdot 0.6 + 0.3 \cdot 0.9 = 0.69$$

If the increase in α through the aeration tank is linear the mean in the first quarter of the tank is 0.72.

(c) Aeration Tank Dimensions

The total tank volume is 0.4 mg(53,300 ft³). Assuming a depth of 15 ft and a width of 20 ft, the length is 175' (44 ft/quarter).

(d) Oxygen Saturation

Operating temperature = 30°C; $f = 0.95$; assumed transfer efficiency 8 o/o; submergence on diffusers = 13'.

$$\begin{aligned} C_s &= fC^* \left(\frac{P_b}{29.4} + \frac{\alpha t}{42} \right) \\ &= 0.95 \cdot 7.63 \left(\frac{20.3}{29.4} + \frac{19.6}{42} \right) = 8.4 \text{ ppm} \end{aligned}$$

(e) Required $K_L a$ - first quarter

Employing an operating dissolved oxygen level of 1.0 ppm

$$k_L a_{30^\circ} = \frac{r}{C_s - C_L} = \frac{47.9}{(8.4 - 1.0)} = 6.47$$

$$\begin{aligned} k_L a_{\text{at } 20^\circ\text{C}} &= K_L a_{(30^\circ\text{C})} \sqrt{\frac{T_1}{T_2} \cdot \frac{U_2}{U_1}} \\ &= 6.47 \cdot 0.88 \\ &= 5.7 \end{aligned}$$

correcting for

$$k_L a = 5.7 / 0.72 = 7.92$$

(f) Diffuser Spacing

The operating data for a particular diffuser in water at 20°C and 13 ft submergence is as follows:

<u>Air flow, scfm/unit</u>	<u>K_{La}</u>	<u>V_t</u>
4	610	
5	800	
6	975	
7	1160	
8	1350	

Designing for 8 cfm/unit

$$K_{La} \cdot V_t = 1350$$

$$V_t = 1350 / 7.92 = 170 \text{ cu ft}$$

$$\text{unit spacing} = \frac{170 \text{ cu ft}}{15 \text{ ft} \cdot 20 \text{ ft}} = 0.565 \text{ ft (6.8 in)}$$

use average spacing of 6 inches

The other sections of tank may be computed in similar fashion. If the computed spacing is beyond design limits the unit depth and width must be adjusted to bring the unit spacing within the specification.

WASTE TREATMENT AT THE SUN OIL COMPANY, LTD.
SARNIA, ONTARIO, REFINERY
Harold F. Elkin
Sanitary Engineer, Sun Oil Company, Philadelphia, Penn.,
and
Gordon R. Henderson
Manager, Sarnia Refinery, Ontario, Sun Oil Company, Ltd.

The combined efforts of industry and the International Joint Commission on The Pollution of Boundry Waters to preserve the water quality of the St. Clair River below the Sarnia, Ontario area have received deservedly wide attention. (1) That these efforts are meeting with success is exemplified by the continued attempts to adhere to I J C objectives by existing and new industries.

Design of Sun Oil Company's Sarnia Refinery in 1952 presented a unique opportunity to construct pollution abatement facilities as an integral part of the plant and to provide for expansion of waste treatment equipment as required by operation experience. This paper will describe the development of this installation and discuss operating results obtained to date.

Sewer and Separator Facilities

Sun's Sarnia Refinery, which was designed to process 15,000 Bbls/day of crude oil, contains completely integrated facilities for control and treatment of plant waste waters. The original installation which was placed in operation in 1953 included an extensive segregated sewer and separator system which served as a basis for current American Petroleum Institute recommended practice for new refineries. (2) Independent drainage systems were installed for the process waste waters, contaminated storm drainage, spent cooling water, uncontaminated storm drainage and sanitary sewage. A sixth sewer system for sulfide-bearing process waters was added in 1955. The process wastes, contaminated storm waters and spent cooling waters are each provided with individual oil-water separators of API design for removal of oil and settleable solids before discharge to the effluent sewer. The total flow of the combined waters in the final effluent sewer averages 14 million gallons per day.

The contaminated storm water separator unit consists of two reinforced concrete parallel single-section chambers, each 20 ft. wide x 160 ft. long x 10 ft. deep. The cooling water separators consist of two parallel single-section chambers, each 20 ft. wide x 180 ft. long x 10 ft. deep. Two 1000 Bbl cone roof tanks are provided for slop oil recovery and three 70 ft. wide x 100 ft. long x 6 ft. deep earth-wall storage basins are available for separator sludge dewatering. Two 10,000 Bbl cone roof tanks are available for ship ballast water disposal.

The process sewer system carries the main oxygen-consuming contaminants in the refinery, averaging 200 GPM or somewhat less than 300,000 ballons per day. This flow contains over 95% of the phenols,

sulfides, mercaptans, emulsified oils and other water-soluble pollutants. These waters come from contact with oil in the plant and include process condensate drains from vessels and towers, pump gland leakage and desalting water. A 10 ft. wide x 45 ft. long x 8 ft. deep concrete single-section oil-water separator was provided for primary treatment of this process waste water. It was anticipated that these process waters would require secondary treatment before discharge, and their segregation was considered a practical initial step. The general flow diagram for segregation of refinery waste waters, from which the Sarnia sewer and separator system was developed, is shown in Figure 1.

The effectiveness of segregation of wastes at their source in aiding subsequent oil-water separation has been established in previous investigations (3), and the above-described Sarnia Refinery drainage system has continuously produced a final net effluent with an oil content of less than 5 ppm.

Secondary treatment for removal of soluble materials is accomplished by flue gas stripping for removal of sulfides followed by biological oxidation in an activated sludge unit for reduction of phenols and other oxygen-consuming contaminants.

Sulfide Stripping Tower

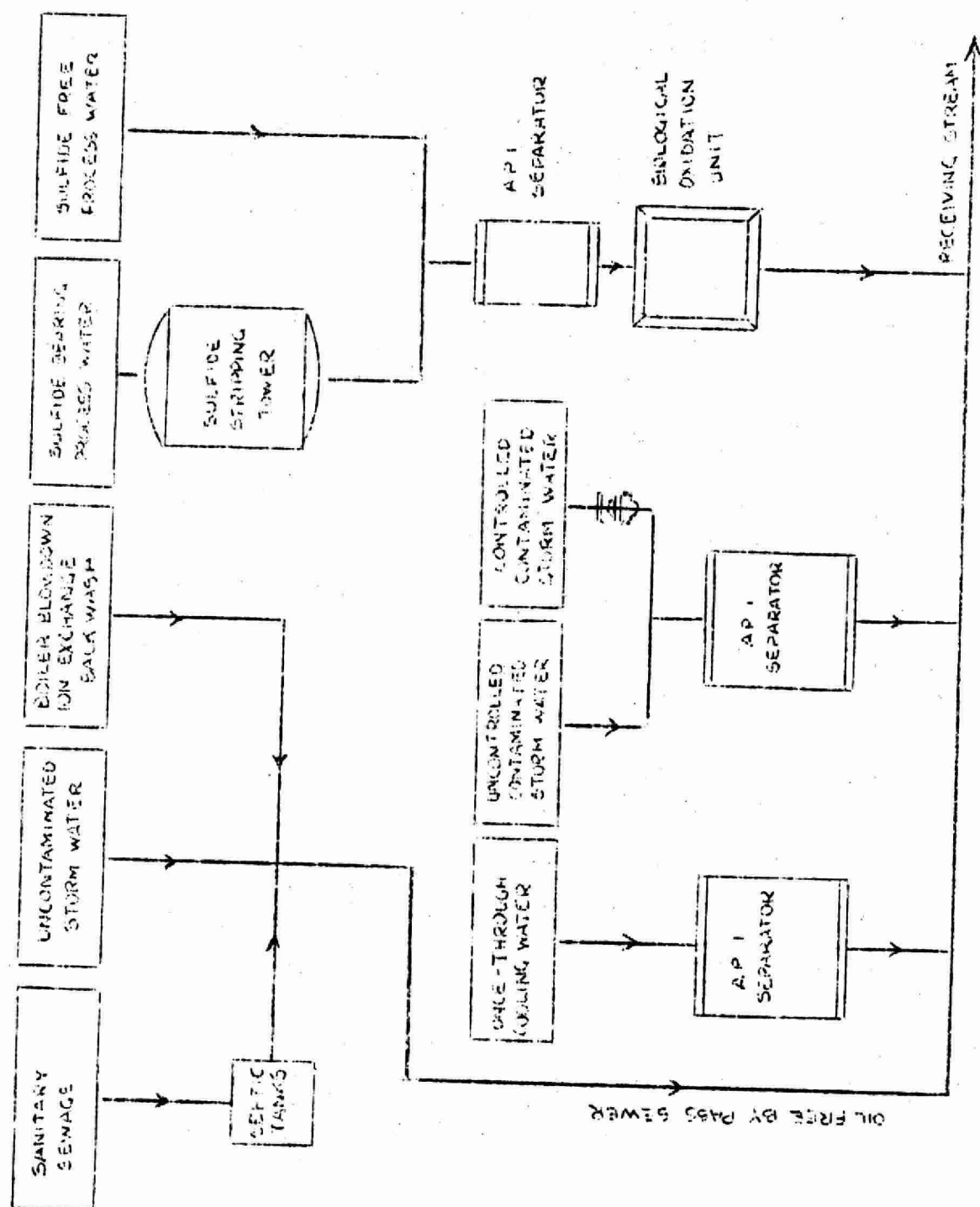
The flow diagram for the sulfide stripping tower installation is shown in Figure 2. This unit utilizes waste flue gas to remove objectionable sulfides and mercaptans from the process water system and to add temperature to the feed water to the subsequent biological treatment unit. Approximately 75 GPM of the process waste waters are collected in an underground concrete oil separating-surge sump and are then charged to the top of the 5 ft.-6 in. diameter by 32 ft. high stripping tower through six 1-1/4 inch full-cone spray nozzles. The injected feed water flows downward against a continuous rising column of approximately 155,000 SCFH of 950° F flue gas from the refinery catalytic regenerator to remove over 90% of the sulfides from the feed water. Operation data for the stripping tower during recent months is shown in Figure 3 and summarized in Table 1.

This stripping tower is unique in refinery practice in several respects. Because flue gas was available only at the low pressure of 2 psig, the entire tower and gas-piping system had to be designed for a maximum pressure drop of 1.5 psig. A tower design was therefore developed consisting only of a distribution header with the six spray nozzles and a demisting section. No tower packing or trays were installed. The internal walls of the tower shell were lined with 2 inches of gunnited high alumina-vermiculite cement for corrosion resistance. Because of the intimate contact of the sprayed feed water with the flue gas, sulfide removal has been satisfactory even at low temperatures as noted in the data of Figure 3. It has therefore not been necessary to augment the flue gas with stripping steam to maintain performance.

The stripping tower desulfurized bottoms are heat exchanged with the sulfide-rich charge water and then flow with the other process waste waters to the process separator for further oil removal before additional treatment.

FIGURE 1

FLOW DIAGRAM FOR SEGREGATION AND TREATMENT OF WASTE WATERS
 GARNER OIL REFINERY - SUN OIL COMPANY



23.

FIGURE 2 FLOW DIAGRAM FOR SULFIDE STRIPPING TOWER - 1955

SARNIA REFINERY - SUN OIL COMPANY

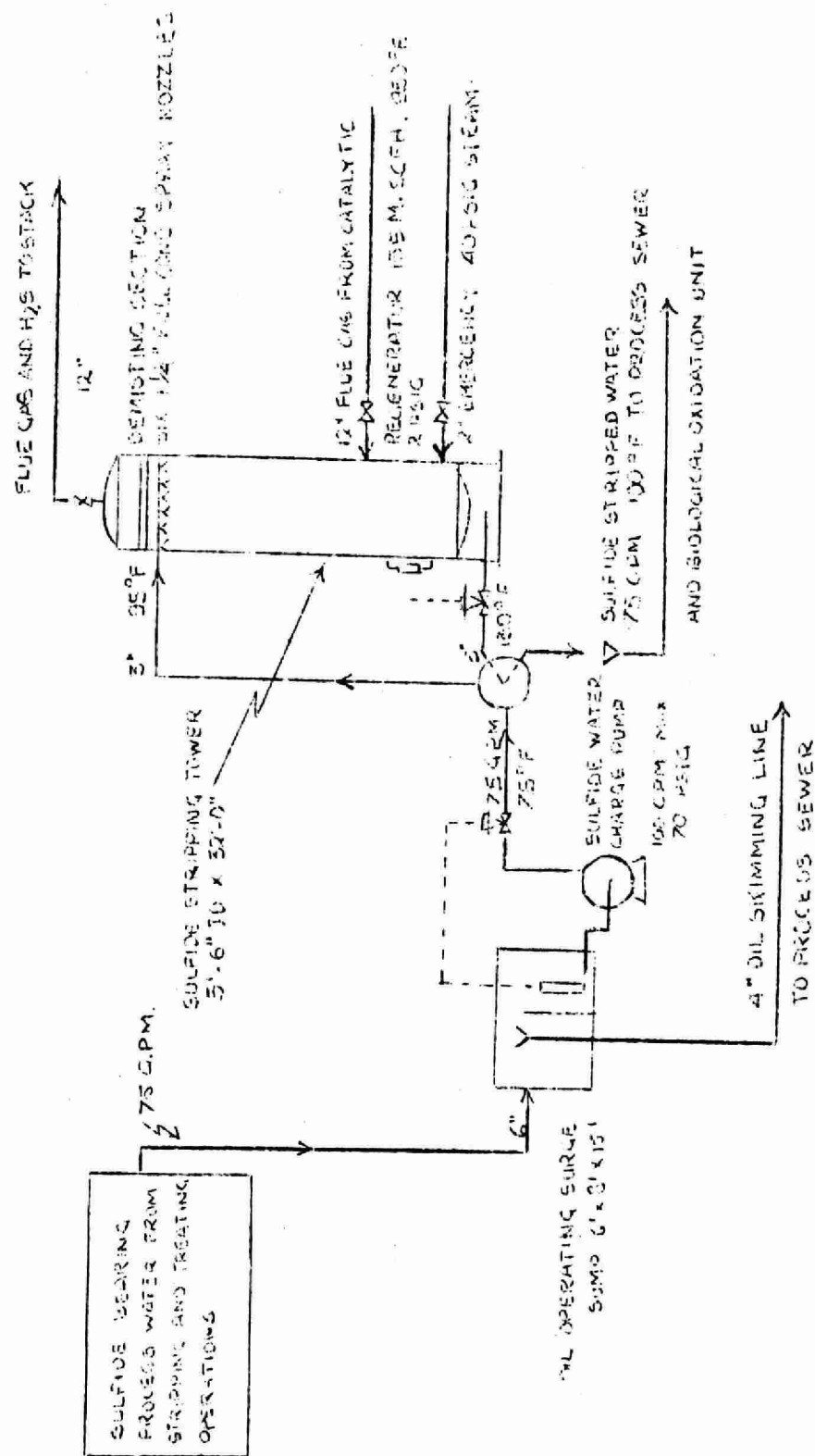
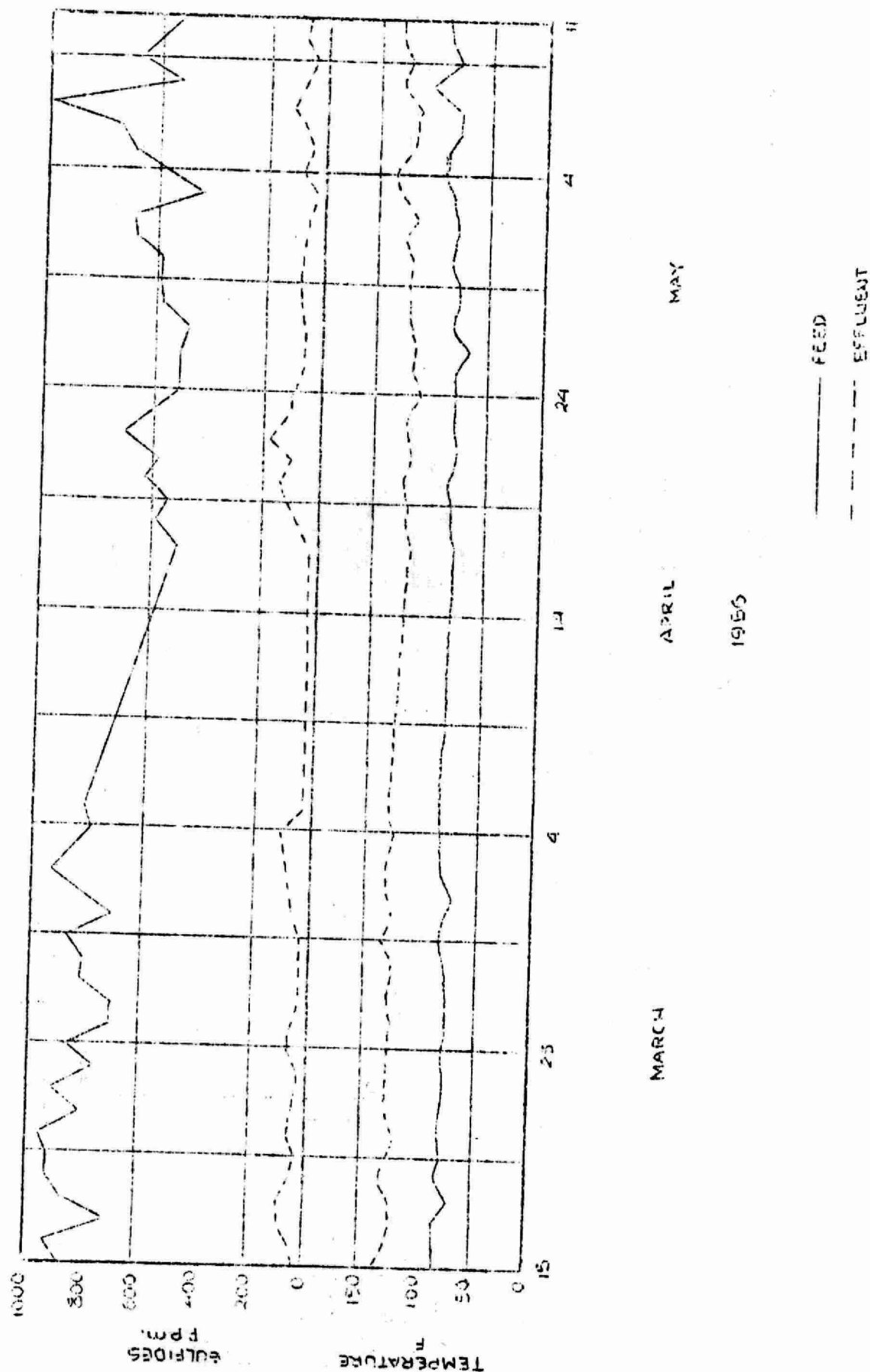


FIGURE 3 - SULFIDE STRIPPING TOWER OPERATION
SARINIA REFINERY SUI OIL COMPANY



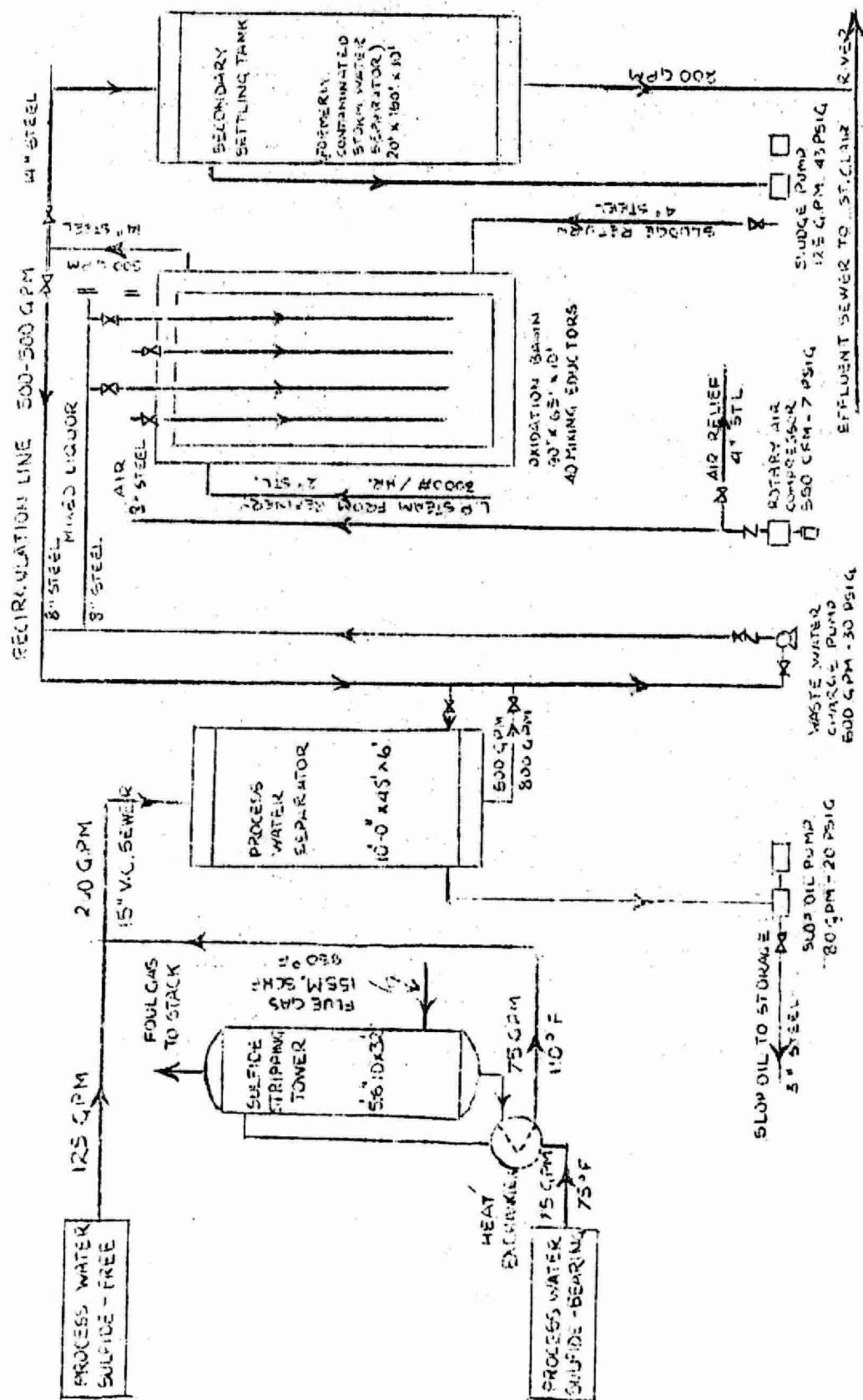
Biological Oxidation Facilities

Sun Oil Company initiated operation of commercial-scale biological oxidation for refinery waste waters at the Sarnia plant in 1953. A modified activated sludge unit was installed to oxidize phenols and other organic contaminants in the process waste waters. The activated sludge process was selected over competitive methods of treatment because of relative simplicity of construction, low investment cost, minimum space requirements, availability of low-cost electric power and anticipated high operation efficiency. The utilization of sludge-recirculation in the aeration basin for metabolic oxidation (endogenous respiration) of excess bacterial growths, thereby eliminating separate sludge digestion equipment, represented another advantage of the activated sludge process.

When Sun Oil developed plans for the biological treatment unit, helpful information was made available by the Dow Chemical Company (4) and Imperial Oil Limited (5, 6) who had plant and pilot-scale experience respectively with biological removal of phenols. Construction of the bio-oxidation unit was expedited by the use of the process sewer and separator system, in which the phenolic waters had already been segregated, and by utilizing other existing equipment and piping already in place. As shown on Figure 4, Flow Diagram of Phenol Oxidation Facilities, the aforementioned sulfide stripping tower and process separator are necessary initial steps in feed water conditioning. The 200 GPM flow from the process separator is transferred by a self-priming centrifugal pump, rated at 500 GPM and 35 psig discharge pressure, to an earth-wall oxidation basin. The aeration basin has top dimensions of 90 ft. long x 65 ft. wide x 10 ft. deep. The bottom half of the side-walls of the basin are surfaced with a 2" layer of cement grout to minimize erosion. The fresh feed water and recycle (mixed liquor volume totals 500 GPM) enter the bottom of the basin through a nest of 40 mixing eductors. A rotary blower, rated at 500 cfm at 7 psig, supplies air to the eductors providing oxygen and intimate mixing. The overflow from the aeration basin flows through a 14" peripheral slit-pipe flume to one section of the contaminated storm water separator originally designed for oil removal service. This separator is equipped with continuous flight scrapers and serves as a secondary settling tank for bacterial sludge. A positive displacement sludge pump, rated at 125 GPM and 43 psig, returns the settled bacterial floc to the oxidation basin. Clarified effluent flows from the secondary separator to the main uncontaminated water system discharging to the St. Clair River. Piping has been provided to recirculate all or a portion of the aeration basin effluent during periods of low volume feed and when refinery process operations are shut down for normal maintenance.

The modified activated sludge facilities were placed in operation in November, 1953, in time to treat the first waste waters from the refinery. Two tank truck loads of concentrated bacterial sludge from the Dow Chemical Company waste treatment plant at Midland, Michigan, were obtained for initial seeding. Bacterial oxidation of phenol began

FIGURE 4. FLOW DIAGRAM FOR PHENOL OXIDATION FACILITIES - 1955
SARNIA, ONTARIO REFINERY - SUNCIL COMPANY



within the first few hours. The approximate first cost of the new facilities was \$40,000. This does not include the value of the previously installed equipment including the process separator, collecting system and the secondary settling tank nor does it include the recently installed sulfide stripping tower.

Experience through the first two years of operation indicates that an average phenol content in the process waste feed of approximately 100 lbs/day can be oxidized satisfactorily. Daily loadings as high as 200 lbs. of phenol have been removed with no loss in efficiency. Numerous mechanical difficulties and variations in feed water quality interfered with continuous efficient performance of the bio-oxidation unit during the first year of operation. High alkalinity and sulfide concentrations in the feed water have been corrected by the above mentioned flue gas stripping tower. Excessive sulfides formerly exerted a high chemical oxygen demand on the system and proved toxic to the bacterial colony. Efficient operating conditions include a bacterial sludge volume index of 4-6%, a temperature range of 70-90° F and a pH range of 6.0-9.0. Experience indicates that the process will operate with a temperature as low as 60° F but with reduced efficiency. Dissolved and emulsified oil concentrations as high as 150 ppm, phenol concentrations up to 200 ppm and sulfide concentrations up to 50 ppm have had no pronounced harmful effect on biological activity, although higher values can seriously injure the bacterial sludge. High oil content in the feed water, although apparently not toxic to the organisms, is adsorbed on the biological floc and floats the mixture to the surface of the basin, thereby removing organisms from the process. It is believed that some oil is partially oxidized. Steam is introduced for temperature control purposes through 1" steel pipe coils with submerged exhausts into the oxidation basin. A direct-contact 2,500,000 BTU/HR water heater has been installed above the surface of the basin as an auxiliary source of heat.

In the case of all of these factors, it has been found important to avoid sudden or shock loadings in influent characteristics. It has been observed that organisms can remain inactive for several days under adverse conditions, then regain their former activity with the return of normal temperature and food supply. The hardness of the bacterial colony is best exemplified by the fact that re-seeding of the unit from a neighboring sewage plant has been required only once since original start-up, following a scheduled refinery maintenance shut-down. During other periods when refinery units were not operating and there was no continuous flow of waste process water, mixed liquor was recirculated at the oxidation basin and chemical-grade phenol was used to continue the food supply.

Air requirements of the aeration basin are supplied by 40 jet eductors mounted above the floor. Each aerator supplies 50 pounds of oxygen or a total of 2,000 lbs./day to the waste water to oxidize the average 130 lbs./day (maximum 350 lbs./day) of phenol, considerably in excess of the theoretical stoichiometric ratio of 2.4 to 1.0. The aeration tank loading is equivalent to 4 pounds of phenol per 1,000 cubic feet of tank volume, and the applied air rate is equivalent to 0.1 cubic feet per minute per square foot of aeration surface. Total power requirements of the pumps and blower amount to 60 HP.

When the above-mentioned problems of temperature and influent characteristics were corrected, operation of the biological treatment unit produced a continuously satisfactory effluent. Recent operating data are presented graphically on Figure 5. A summary of average, maximum and minimum phenol contents of biological treatment unit influent, effluent and final combined refinery discharge are tabulated in Table 2. As evidenced herein, good operation is characterized by over 95% removal of phenols.

One of the remaining operating difficulties still to be corrected is the continuing use of the rectangular oil-water separator as the secondary biological sludge settling tank. This equipment is oversized and not of conventional design for bacterial floc recovery. Although oxidation efficiency is not seriously affected, a suitably-designed replacement tank is under consideration.

Annual operating and maintenance expense for the biological oxidation unit during the past year are summarized in Table 3. The unit cost of \$0.45/lb. of phenol removed is considered moderate when compared with alternate chemical treating or incineration procedures.

The two years of operation of the Sarnia unit indicates that the activated sludge process is applicable to refinery waste waters. Despite early operating difficulties, the equipment has displayed good reliability when supplied with a consistently acceptable feed water and has provided a satisfactory solution to the plant organic pollution problem.

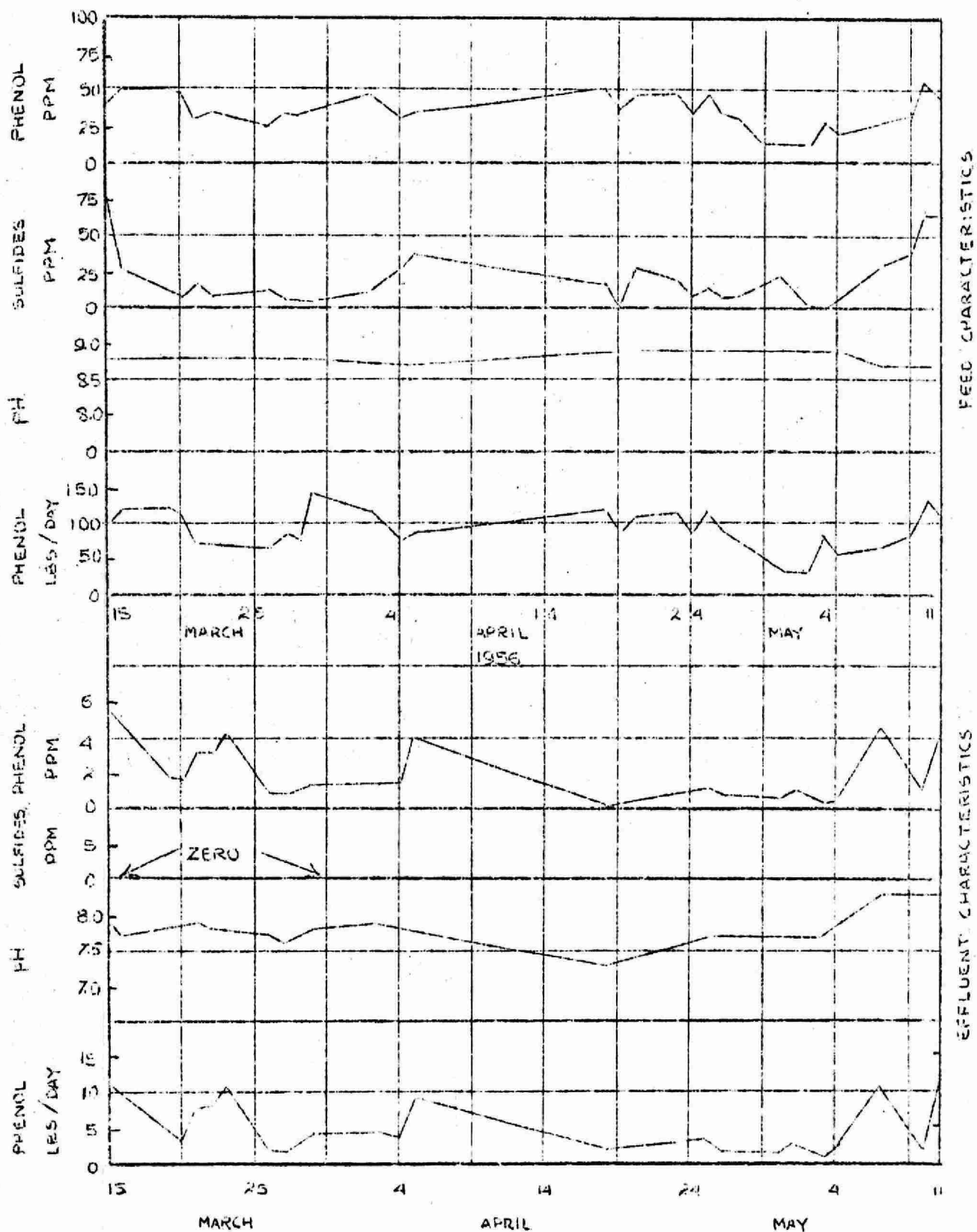
Conclusion

The opportunity of designing pollution control facilities as an integral part of plant operation equipment represents an effective approach to treatment requirements. Installing the segregated sewer and separator system during initial Sarnia Refinery construction made possible the subsequent rapid and economical installation of the biological oxidation unit to treat a limited volume of concentrated waste waters.

Acknowledgements

The authors wish to express appreciation to Mr. Nestor Czornyj, Chief Product Technician of the Sarnia Refinery Laboratory, Sun Oil Company, Ltd. for his assistance in collecting the operating data reported herein. The helpful and informative comments during construction and initial operation by Captain A. V. DeLaporte of the Ontario Department of Health, Messrs. A. D. McRae of Imperial Oil Limited and T. J. Powers of Dow Chemical Company are also gratefully acknowledged.

FIGURE 5
BIOLOGICAL OXIDATION PLANT OPERATION
SARNIA REFINERY - SUN OIL COMPANY



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TABLE 1
SULFIDE STRIPPING TOWER OPERATION DATA-SUMMARY*
SARNIA REFINERY - SUN OIL COMPANY

	<u>STRIPPER INFLUENT</u>			<u>STRIPPER EFFLUENT</u>			<u>PER CENT REMOVAL</u>
	<u>MAX</u>	<u>MIN</u>	<u>AVG</u>	<u>MAX</u>	<u>MIN</u>	<u>AVG</u>	<u>AVG</u>
FLOW - GPM	-	-	75	-	-	75	-
TEMPERATURE-°F	109	68	75	134	108	122	-
SULFIDES-ppm	1000	424	705	174	23	63	91.0%

*Data based on March-May, 1956 operation

TABLE 2
BIOLOGICAL OXIDATION PLANT OPERATION DATA-SUMMARY*
SARNIA REFINERY - SUN OIL COMPANY

	PLANT INFLUENT			PLANT EFFLUENT			PER CENT
	<u>MAX</u>	<u>MIN</u>	<u>AVG</u>	<u>MAX</u>	<u>MIN</u>	<u>AVG</u>	<u>REMOVAL</u> <u>AVG</u>
FLOW - GPM	250	150	200	250	150	200	-
pH	8.9	8.3	8.8	8.2	7.3	7.8	-
SULFIDES-ppm	76	0	22	0	0	0	-
SULFIDES-lbs/day**	182	0	55	0	0	0	100%
PHENOL-ppm	56	14	41	4.8	0.4	1.9	-
PHENOL-lbs/day**	135	34	98	12	1	4.5	95.5%

* Data based on March-May, 1956 operation.
** Based on average flow rate.

TABLE 3
ANNUAL COST OF PHENOL REMOVAL - 1955
BIOLOGICAL OXIDATION - SARNIA REFINERY, SUN OIL COMPANY

OPERATION	\$ 3,000
MAINTENANCE	5,800
ELECTRIC POWER	4,200
STEAM	<u>6,000</u>
TOTAL ANNUAL COST	\$ 19,000

COST PER POUND PHENOL REMOVED	\$ 0.45
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INITIAL CAPITAL INVESTMENT	\$ 40,000
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INDUSTRIAL WASTE CONTROL AT AN ORGANIC CHEMICAL PLANT

R. E. Mills

Naugetuck Chemicals Division of
Dominion Rubber Company Ltd.

Today, the awareness of the public to air and water pollution, means that all companies manufacturing a variety of organic and inorganic chemicals, must take stock of their position in the community with respect to their process wastes.

Naugetuck Chemicals, Division of Dominion Rubber Co., Ltd., is situated in a small town in Central Ontario in the midst of a fine agricultural district; and as a result all wastes are carefully controlled to maintain good relations in this community.

The method of organizing and handling the control problems is most important and is one that requires a great deal of thought. The method used depends upon the type and size of chemical plant concerned and the results obtained are a measure of its success.

The plant foremen and supervisors must give their fullest cooperation and effort in carrying out a waste control program; realizing its importance and taking it to their men. It is in the various production departments where proper education is most valuable in making all employees conscious of the importance of control methods. Education in good housekeeping is most important to reduce spills, floor washings and careless operating procedures which may cause more control problems than the actual processing. A heavy reliance is placed on the foreman and supervisors in this respect.

We believe that personal hygiene on the part of the operators is also important if they are to fully understand our problems of prevention of pollution, both air and water. Our company has just completed a new employee services building which is up-to-date in every respect. The operators will be urged to make full use of these facilities with daily bathing and changing from work clothing to street clothing after each day's work. This clothing will be kept in separate ventilated lockers thus preventing the street clothing from carrying home chemical plant odors.

We believe that employee cooperation in the prevention of pollution will be obtained when they realize the extent to which the company has gone to obtain these objectives.

I - AIR POLLUTION PROBLEMS

Dust Control in The Grinding and Packaging Departments

To control dust from grinding, packaging and loading operations, the cloth collector or bag filter is used. The dust is carried into a cyclone, where the heavier particles, over 5 microns, presettle by the reduction of the velocity of the air stream. The lighter particles rise and form inside vertically-held bags or tubes which are open at one end and closed at the other. The air passes through while the particles are retained on the inside.

The efficiency of this type of collector is measured by the amount of dust in the outlet air. The minimum collectible particle diameter is less than 0.1 microns. (1)

Acid Storage Tanks

The storage of large volumes of acids, alkalies, oils and flammable liquids in a so-called tank farm, may develop a situation under certain atmospheric conditions where the normal "breathing" of tanks under temperature variations causes objectionable fogs, fumes and vapors. This is especially true during the handling of mixed acids containing nitric and sulphuric acids, and hydrochloric acid. If small amounts of ammonia fumes are escaping from a plant process nearby and mix with these acid fumes, a very heavy fog results. To overcome this problem, double traps, containing 93% sulphuric acid which absorbs moisture and sulfur trioxide fumes, have been installed on the 99% sulphuric acid and mixed acid tank vents.

Hydrochloric acid storage tanks have traps on the vents containing weak hydrochloric acid. During pumping to tank cars, the car can be vented back into the storage tank.

The hydrogen chloride gas evolved from one process is effectively absorbed by a Karbate falling-film absorber which produces saleable muriatic acid thus recovering a valuable by-product.

Control Of Hydrogen Sulphide Gas

The quantity of hydrogen sulfide evolved from one plant process is too small to recover the sulphur economically; therefore the disposal of this highly objectionable gas presents a problem. This is solved by forcing the hydrogen sulfide under controlled pressure, through flame arrestors into a furnace at the base of a tall stack. The furnace is fired by a conventional type oil burner. The hydrogen sulfide is converted to sulfur dioxide and the height of the stack must be such that the sulfur dioxide reaches the ground in harmless concentrations. This height can be very easily calculated by using the formula of Bosanquet and Pearson and Sutton. (2)

The average wind velocity, directions, and frequency by directions is a factor, and can be obtained from the Air Services Meteorological Division of the Department of Transport. This may eliminate the necessity of setting up weather equipment if there is such a station in the vicinity of the plant.

Control of Oxides of Nitrogen

These gases create an objectionable condition from an odor, sight and corrosive standpoint. A specially constructed packed ceramic tower was installed with stainless steel ducts which carry the fumes from the process vessels to the tower. A recirculating caustic solution effectively scrubs the effluent gases forming sodium nitrite and nitrate which is subsequently returned to the process. An exhaust fan in the duct from the tower to the atmosphere draws the fumes through the column. This provides some economic return to the process and overcomes a conspicuous nuisance.

General Ventilation

Large air scrubbers are used to reduce dust and take care of general building ventilation. One such installation is a Schneible multi-wash dust collector handling some 4000 c.f.m. of air (3). This consists of a 16 ft. high x 4 ft. diameter vertically placed cylindrical tower, fabricated from a material required by the nature of the dusts and fumes, and of the scrubbing liquid. Inside the tower are six and one-half impingement stages at the top of which is an entrainment separator. At the bottom, the tower terminates in a cone. Dusts and fumes enter the tower tangentially through ducts into the wet cyclone where the heavier particles separate. The absorbing solution is recirculated from a holding tank below, entering the tower above its top impingement place and in its downward motion washes the upcoming air. The horizontal plates and shelves of the impingement stages form a water curtain through which the rapidly whirling air must pass. Organic solvent and phenolic vapors are effectively removed by this device. An exhaust fan on the clean air outlet draws the air through the scrubber. The absorbing solution is recirculated until spent, then renewed; this requires regular testing and is part of the process operation. The electrical set-up on the exhaust fan motor and recirculating pump motor is such that the pump must be going before the fan starts. This prevents ejection of unscrubbed air. The outlet air from this installation is continuously sampled. The suction pressure on the suction side of the exhaust fan draws an air sample from the discharge side of the fan through the two absorbers. This continuous sampler operates whenever the scrubber is in operation. The daily volume of the sample taken here is about 40 cu. ft. per day.

Sampling Methods

To determine the efficiency of any waste control equipment, the exit air from vents, scrubbers and towers must be sampled and analyzed. This is a very important part of waste control.

A typical air sampling unit in operation consists of a 5/8 h.p. gas engine mounted on a small rubber-tired truck. This engine drives a laboratory type vacuum pump, which draws air through a stainless steel wet test meter. Connected to the wet test meter is a trap and two Fisher-Milligan gas samplers. Rubber tubing, or tubing as required by the nature of the air to be handled, draws the air from the sampling point. The gas engine is used for outdoor work and can be interchanged with an explosion-proof electric motor for indoor work. The wet test meter has a capacity of 20 cubic feet per hour. This unit is more adapted to taking "grab" samples at various locations about the plant, at the rate of 10 - 15 cubic feet per hour for 2 - 3 hour's duration,

but could be used for continuous samples if so required.

II - WATER PROBLEMS

Sources, Uses, and Disposal of Plant Waters

In a chemical plant a large volume of water is required daily for cooling, processing, etc. We have two sources from which to obtain our requirements. The first source of supply is from the wells of the town water supply. About 1 million gals. per day are drawn from this source. The second source of supply is from the nearby stream from which about 350,000 gals. are drawn daily.

Water taken from the stream is used for cooling and for boiler plant use. This latter use requires some pretreatment of the water. This auxiliary supply is also available in the event of fire.

All cooling waters are run directly into the stream. General plant wastes are run into ponds or lagoons where solids are allowed to settle out. The build-up of sludge in these ponds is considerable and is removed periodically to provide fill for reclaiming low land. Any oils separating out in waste waters are removed, and if confined to one particular process, are recovered where possible. In any case they are not allowed to enter the stream.

River Water Sampling

The condition of the stream beside the plant is of vital importance. A program for sampling this stream has been set up on a monthly basis. Sampling is carried on throughout the year since this stream does not usually freeze during the winter. Samples are taken up stream from the plant, at the plant, and down stream from the plant. Samples are taken also at points 1 mile and 3 miles below the plant, and above and below the confluence of the river into which the stream empties, about 5 miles from the plant. During the sampling the stream is inspected for algae and fish life which is a visual indication of the condition of the stream. The temperature of the stream is recorded at each sampling point. Weather conditions and stream flow are indicated at each sampling time.

These water samples are compared for:-

- (1) pH which should be between 6.7 and 8.3 (4). This limits the quality of the water effluent from the plant to pH ranges dependent upon the volume of flow of the stream and volume of the waste.
- (2) Chemical oxygen demand; is the oxygen that will be demanded by a waste as measured by chemical oxidation. This value is an important index for stream and industrial waste studies and is useful when the biochemical oxygen demand cannot be determined.(4)

- (3) Dissolved oxygen; adequate dissolved oxygen is necessary for the existence of fish life and other aquatic organisms. It has been stated that the dissolved oxygen in surface waters which are unpolluted range from about 5 ppm to 9 ppm (5). Suffocation of fish results from a low dissolved oxygen concentration.
- (4) Taste, odor, and turbidity. In addition to these, analyses are carried out for the detection of any particular contaminant that may be expected dependent upon the products being made at the plant at the time of sampling. This practice will indicate leaks or spills.

Samples are also collected from the main plant sewers, from individual sewers and from the stream into which wastes are discharged. Samples of waste from the main waste streams should be a composite sample taken over a 24-hr. period. The automatic sampler used for this purpose, contains 28 bottles in a tray and the waste is drawn from the sewer continuously by a Sigma pump. The rate of flow of the waste is adjusted so that one bottle is filled per hour. Each bottle is therefore representative of the flow through the sewer for that particular hour and the full tray of bottles is representative of the contents of the sewer over a 24 hour period.

III - TREATMENT OF PHENOLIC AND 2,4-D WASTE WATERS

Hyflo Super-cell Process

During the 1950-51 production season of 2,4-Dichlorophenoxyacetic Acid (2,4-D) the waste water was treated by passing it through a Sparkler filter using supercell Hyflo Filter Aid which removed the entrained solvent only. The waste was then partially neutralized with soda ash and pumped to a closed pit.

Activated Carbon Process

During the 1951-52 season activated carbon was used to treat the 2,4-D waste water. The waste water was first filtered through the Sparkler Filter to remove the entrained solvent as already mentioned. This filtered waste water was then passed down through a bed of activated carbon by spraying through a distributor to spread the flow. A rotameter was placed in the feed line to measure the rate of flow. The treated water was then partially neutralized with soda ash and pumped to a closed pit.

The activated carbon tank consisted of a 6 foot by 3 foot diameter wooden tank open at the top. On the bottom of the tank was placed 12 inches of gravel. Immediately above the gravel was placed a $\frac{1}{4}$ " mesh iron screen to support the 600 lbs. of activated carbon. For the removal of the spent carbon, which was disposed of by burying, a 15 x 15 inch door was installed, 15 inches from the bottom of the tank. The space taken up by the 600 lbs. of carbon was 34 inches deep by 34 inches in diameter or 18 Cu.Ft. of carbon. The average rate of flow of waste water into the carbon was 7 Imperial Gallons per minute. Therefore, the linear velocity of liquid through the carbon was 2.14 inches per minute. The recommended rate by our Development Department was 2.7 inches per minute.

The treated outlet water from the tank flowed through a leg which would maintain a minimum of 12 inches depth of liquid on the 34 inch depth of carbon. The type of carbon used was Pittsburg G.W., 4 x 20 mesh activated carbon.

The curve shown in Figure 1 indicating parts per million of 2,4-D and Dichlorophenol (DCP) as the volume of waste water treated indicates that the carbon was spent after 5000-6000 gallons of waste water were treated.

It was suggested that if the carbon bed had been of greater depth, say 5 feet instead of 3 feet, the concentration of DCP and 2,4-D in the treated waste water would have been less.

If we consider that the carbon was spent after 6000 gallons of waste water had passed through then the cost of treatment would have been \$6.00 per lb. of phenol removed. Since this was the cost of activated carbon only this method was considered too expensive to be continued. Also the use of activated carbon on the throw-away basis made the disposal of the spent carbon a problem.

Alkaline Chlorination Process

Information was obtained in 1951 which enabled us to establish a process for destroying DCP by means of oxidation in an alkaline medium by chlorine. Caustic soda was selected then as the neutralizing material. This well known alkaline chlorination process is still essentially the method of treatment used today. Some modifications have been made to handle the increased volume of waste due to increased production. The waste water is treated in a cement sump. A portion of the recirculation flow is through a pH cell which operates a pH recorder-controller unit feeding caustic soda solution to the sump to maintain pH control. The alkalinity is controlled in a pH range of 9-11. A chlorinator injects chlorine water to the sump at a volume sufficient to obtain a chlorine residual of 200 ppm in the treated waste water. This is then pumped to a closed pit. A 97% reduction of DCP is obtained by this process. This method of treating 2,4-D waste-water presently, cost \$1.02 per lb. of phenol destroyed. This is the cost of Caustic Soda and Chlorine only.

The volume of 2,4-D waste has increased sufficiently since 1952 to justify the investigation of some cheaper method of treatment.

As a result of laboratory investigation the use of dolomitic lime instead of caustic soda has been considered. This method compares very favourably with the caustic soda chlorination with respect to DCP reduction, Figure 2, giving a reduction of 98%. The two major problems which would arise if this method were adapted would be; (a) To find some cheap method of dewatering the resulting calcium sulfate sludge. (b) To dispose of the sludge in a satisfactory manner.

Acid chlorination of the waste water (pH 1.5) would not be considered too satisfactory since a reduction of only 83% DCP was obtained in the laboratory, Figure 2, Corrosion of equipment would be high resulting in increased maintenance costs.

FIGURE 1. ACTIVATED CARBON TREATMENT OF 2,4-D WASTE WATER

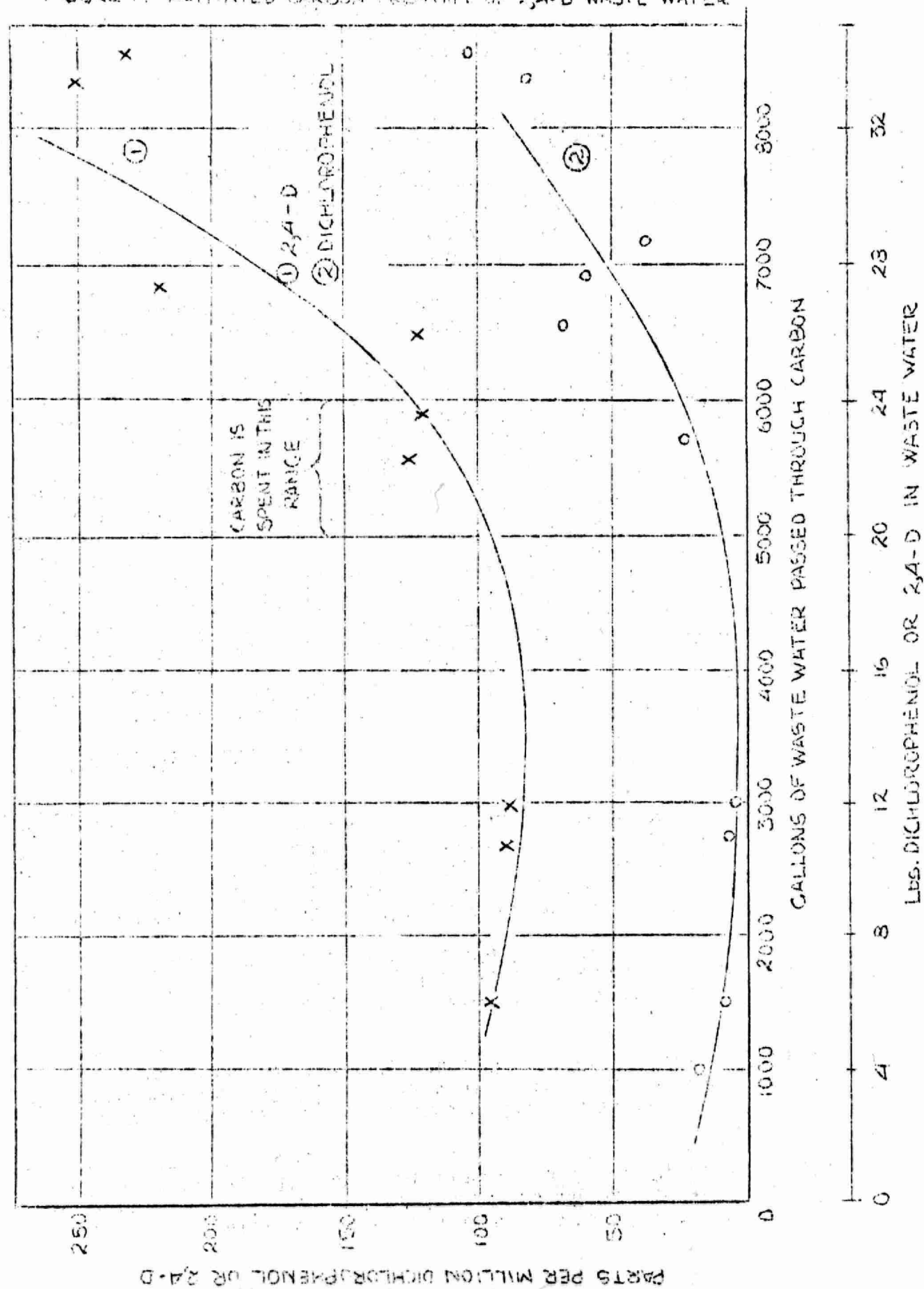
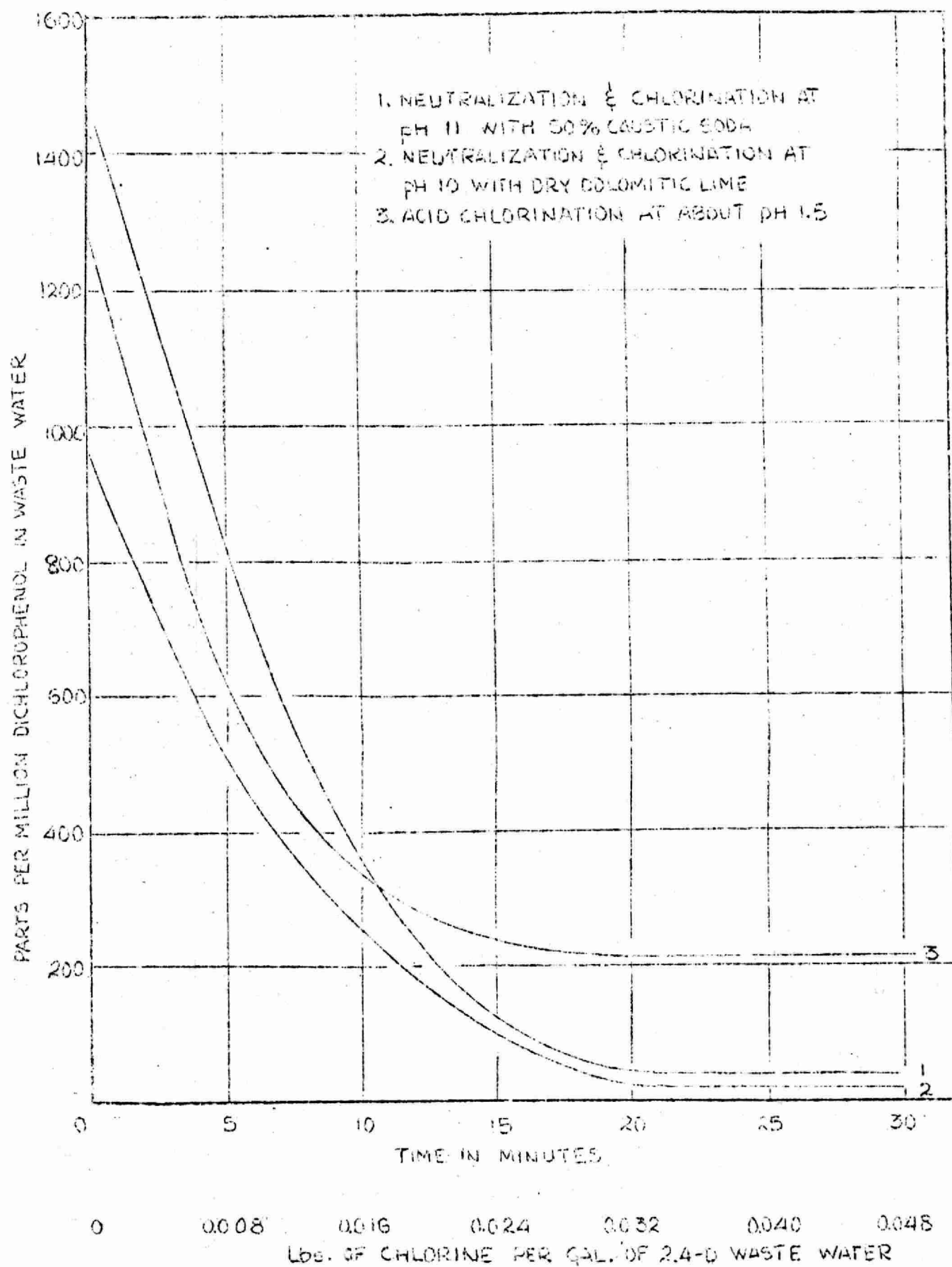


FIGURE 2 CHLORINATION OF 2,4-D WASTE WATER



Bio-Oxidation Process

The cost of destroying a pound of phenol by the various known methods has been estimated to be: Bio-oxidation \$0.30, Ozone \$1.00, Chlorine \$2.30, Chlorine Dioxide \$7.00, and Incineration \$5.30 (7). As already mentioned we have found that the cost of the raw materials required for the removal of a pound of phenol in our own wastes to be as follows: Activated Carbon \$6.00, Alkaline Chlorination \$1.02.

Since it is our intention to reduce still further the present high cost of treating our phenolic and 2,4-D wastes and to do away with the present method of discharging waste waters to closed pits, we propose to construct a biological trickling filter as shown in the flow diagram, Figure 3. The filter is expected to be in operation some time this summer. It is expected to handle only phenolic wastes from processes other than the 2,4-D process and a portion of the 2,4-D waste water.

We are collaborating with the Dow Chemical Co., on this project, and are using their Dowpac H.C.S. as packing media for the column of the trickling filter, instead of blast furnace slag usually used in conventional trickling filters. The bulk characteristics of the two trickling filter media are shown on Table I.

Some preliminary work has been done in the laboratory using model activated sludge units. The purpose of this work was to determine whether our plant wastes can be fed to bacterial slimes without preliminary treatment of the particular waste or toxic affects of the waste on the bacteria due to the presence of traces of other contaminants in the waste water.

These units were devised in such a manner as to permit continuous feeding of synthetic and plant wastes and continuous removal of the treated waste. Each unit was seeded with activated sludge from a local sewage plant.

The units were operated with continuous feeding 24 hours a day, 7 days a week. Feeds were changed, samples for analysis taken, temperatures recorded, and any changes in operating procedure made at the same time each day.

Feed waters and effluents were analysed for chemical oxygen demand and where possible the individual contaminating component in the waste. Nitrogen as ammonium nitrate and phosphorous as potassium di basic phosphate were added to the feed to give an approximate C:N ratio of 20:1 and C:P ratio of 30:1.

Each unit was aerated continuously 24 hours a day at an average aeration rate of 1400 Cu.Cm./Min. The feed rate was adjusted to about 6 litres per day giving a retention time of approximately 16 hours.

A summary of the composition of the various feeds, the conditions of treatment and effectiveness of the treatment is given on Table II for synthetic plant wastes. A similar outline is given on Table III for actual plant wastes. By synthetic plant wastes we mean a waste made up of the pure component expected to be the major contaminant in a specific plant waste from a particular plant process. Tap water was used for dilution. Nitrogen and phosphorous were added as required.

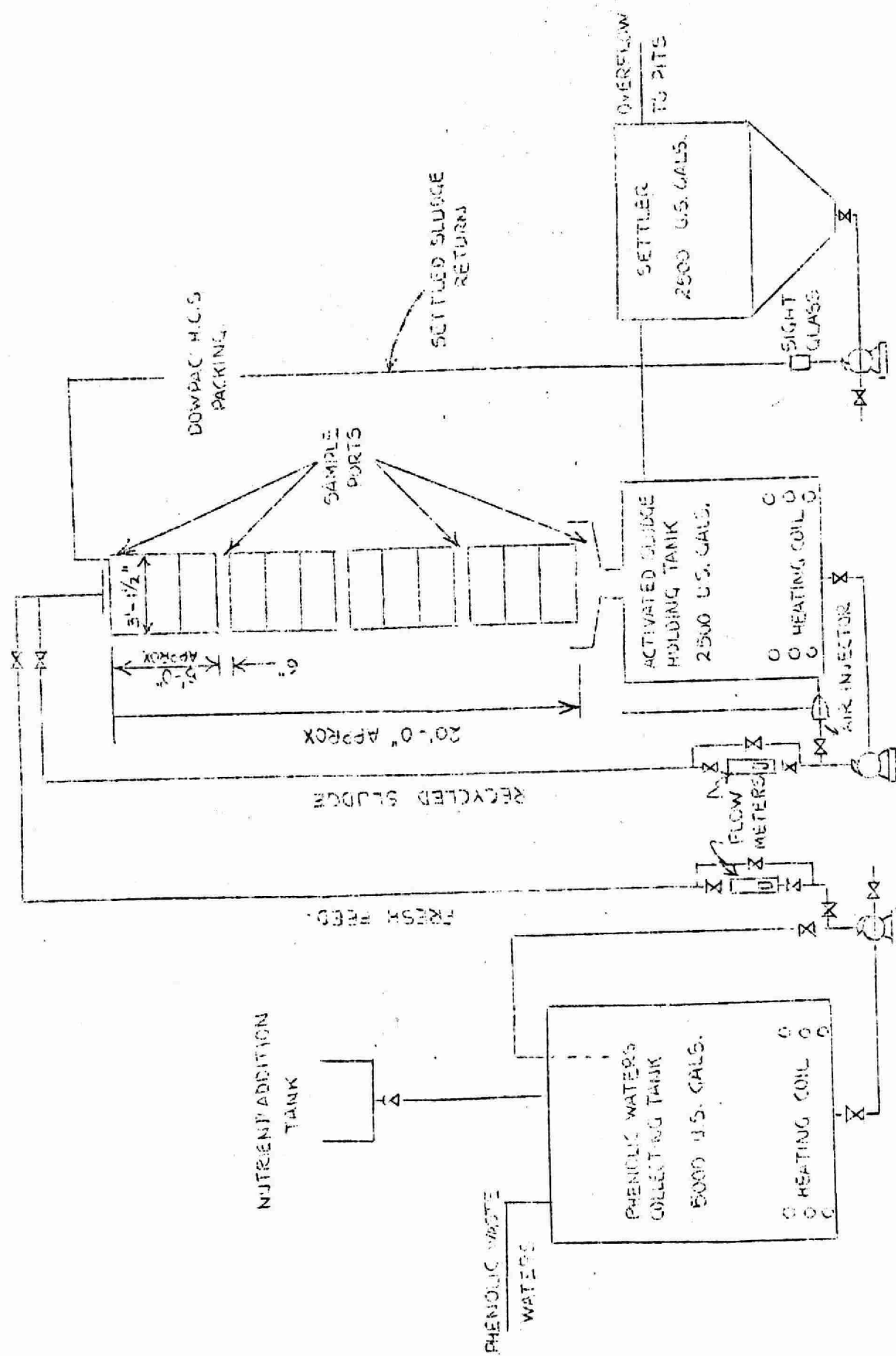


FIGURE 3 PROPOSED PILOT PLANT BIO-OXIDATION TRICKLING FILTER

Where the treatment of 2,4-D waste was concerned a bio-assay method (8) was carried out on the effluent from the laboratory activated sludge units to determine the removal of the 2,4-D. The information obtained from this work will allow us to feed certain of the wastes investigated with the assurance that these wastes will not be toxic to the bacteria, which will grow on the trickling filter. This information will also enable us to predict the strength at which to feed the wastes and hence the dilution required. Dilution will be achieved by recirculation on the trickling filter as shown in Figure 7.

CONCLUSION

The foregoing is an outline of a few of the preventative and corrective measures that have been taken in the waste control program at Naugatuck Chemicals in Elmira. A brief description of the past and present treatment of our Phenolic and 2,4-D wastes has been given. Wastes of this type are being treated by the alkaline chlorination method which, although effective, has a cost element attached which we would like to reduce.

Some of the preliminary work for our proposed biological trickling filter has been outlined. We feel that bio-oxidation of this type is the most satisfactory and economical method to date for treating our phenolic and 2,4-D waste waters.

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- (2) Bosanquet, C. H., and Pearson, J. L., "The Spread of Smoke and Gases from Chimneys," Trans. Faraday Soc. 32.1249 (1936).
- (3) Claude, B., Schneible Company, Detroit 32 Michigan - The Multi-Wash Senior Collector.
- (4) Standard Methods for Examination of Water, Sewage and Industrial Wastes 10th Ed. 1955.
- (5) Manual on Disposal of Refinery Wastes; Vol. III 2nd Ed.(1951)

- (6) Majowski F., "The Treatment of Wastes at the Rohm & Hass Company." Proceeding of the 8th Ind. Waste Conference, Purdue University.
- (7) Ross W. K., Sheppard A.A., "Biological Oxidation of Petroleum Phenolic Waste Waters." "Proceeding of the 10th Ind. Waste Conference, Purdue University.
- (8) Reedy D., Grant U. Q., " A Rapid Sensitive Method for the Determination of Low Concentrations of 2,4-Dichlorophenoxyacetic Acid in Aqueous Solutions." Botanical Gazette No. 1 109 (1947)

TABLE I

BULK CHARACTERISTICS OF TWO
TYPES OF TRICKLING FILTER MEDIA *

<u>Packing</u>	<u>Units</u> <u>/Cu. Ft.</u>	<u>Units Weight</u> <u>Lbs./Cu.Ft.</u>	<u>Surface Area</u> <u>Sq.Ft./Cu.Ft.</u>	<u>Void Space</u> <u>%</u>
Dowpac HCS	2.0	3.8	25	94
Blast Furnace Slag 3-3/4" x 3-1/8 x 2-1/2"	51	68	20	49

Mills

* Dowpac FN-90 and Dowpac HCS. - Bulletin Published by the
 Dow Chemical Company.

TABLE IISYNTHETIC PLANT WASTESSYNTHETIC PHENOLIC WASTE

<u>Composition of Feed</u>	<u>Min.</u>	<u>Max.</u>	<u>Av.</u>
pH	7.4	7.9	7.5
Temperature (°F.)	68	75	71
C.O.D. (ppm)	141	346	260
Phenol (ppm)	30	140	95
<u>Conditions of Treatment</u>			
Aeration (Hrs./day)	-	-	24
Aeration Rate (Cu.Cm./Min.)	-	-	1400
Retention Time (Hrs.)	12	19	16
<u>Effectiveness of Treatment</u>			
pH	7.5	8.4	8.0
C.O.D. Removal (%)	91	100	97
Phenol Removal (%)	99	99	99

SYNTHETIC DICHLOROPHENOL (DCP) WASTE

<u>Composition of Feed</u>	<u>Min.</u>	<u>Max.</u>	<u>Av.</u>
pH	8.0	8.4	8.2
Temperature (°F.)	67	75	70
C.O.D. (ppm)	162	221	187
DCP (ppm)	105	177	153
<u>Conditions of Treatment</u>			
Aeration (Hrs./Day)	-	-	24
Aeration Rate (Cu.Cm./Min.)	-	-	1400
Retention Time (Hrs.)	19	32	24
<u>Effectiveness of Treatment</u>			
pH	8.0	8.3	8.2
C.O.D. Removal (%)	78	89	84
DCP Removal	99	99	99

TABLE II (Cont'd)

SYNTHETIC WASTE CONTAINING ONLY 2,4-D

<u>Composition of Feed</u>	<u>Min.</u>	<u>Max.</u>	<u>Av.</u>
pH	8.5	8.5	8.5
Temperature (°F.)	65	74	68
C.O.D. (ppm)	237	281	249
2,4-D (ppm)	194	230	204
<u>Conditions of Treatment</u>			
Aeration (Hrs./day)	-	-	24
Aeration Rate (Cu.Cm./Min.)	-	-	1400
Retention Time (Hrs.)	19	27	23
<u>Effectiveness of Treatment</u>			
pH	6.1	7.7	6.8
C.O.D. Removal (%)	63	87	74
2,4-D Removal (%)	94	97	96
Bio-Assay (Cucumber Seed Test)	-	Normal Growth	

SYNTHETIC 2,4-D WASTE

<u>Composition of Feed</u>	<u>Min.</u>	<u>Max.</u>	<u>Av.</u>
pH	7.8	7.9	7.9
Temp. (°F.)	76	78	77
2,4-D (ppm)	153	156	155
DCP (ppm)	120	138	133
C.O.D. (ppm)	271	300	285
<u>Conditions of Treatment</u>			
Aeration (Hrs./day)	-	-	24
Aeration Rate (Cu.Cm./Min.)	-	-	1400
Retention Time (Hrs.)	19	32	25
<u>Effectiveness of Treatment</u>			
pH	8.0	8.0	8.0
2,4-D Removal (%)	93	99	96
DCP " (%)	94	100	96
C.O.D. " (%)	75	76	75
Bio-Assay (Cucumber Seed Test)	0 - 5 ppm 2,4-D		

TABLE III
ACTUAL PLANT WASTES

PLANT WASTE FROM THE DICHLOROPHENOL PROCESS

<u>Composition of Feed</u>	<u>Min.</u>	<u>Max.</u>	<u>Av.</u>
pH	7.5	9.7	8.5
Temperature (°F.)	65	76	70
C.O.D. (ppm)	161	955	427
DCP (ppm)	82	652	391
<u>Condition of Treatment</u>			
Aeration (Hrs./day)	-	-	24
Aeration Rate (Cu.Cm./Min.)	-	-	1400
Retention Time (Hrs.)	20	80	32
<u>Effectiveness of Treatment</u>			
pH	6.3	8.4	7.7
C.O.D. Removal (%)	75	95	82
DCP Removal (%)	96	100	99
Bio-Assay Method	-	-	Normal Growth

PLANT WASTE FROM THE 2,4-D PROCESS

<u>Composition of Feed</u>	<u>Min.</u>	<u>Max.</u>	<u>Av.</u>
pH	7.6	8.3	7.9
Temp. (°F)	69	74	72
C.O.D. (ppm)	896	1046	972
DCP (ppm)	122	148	138
<u>Conditions of Treatment</u>			
Aeration (Hrs./day)	-	-	24
Aeration Rate (Cu.Cm./Min.)	-	-	1400
Retention Time (Hrs.)	17	32	27
<u>Effectiveness of Treatment</u>			
pH	8.6	8.8	8.7
C.O.D. Removal (%)	15	41	28
DCP Removal (%)	94	97	95
Bio-Assay Method	No growth of cucumber seeds.		

TABLE III (Cont'd)PLANT WASTE CONTAINING PHENOL

<u>Composition of Feed</u>	<u>Min.</u>	<u>Max.</u>	<u>Av.</u>
pH	6.1	8.8	7.8
Temp. (°F.)	68	77	72
Phenol (ppm)	42	1520	606
C.O.D. (ppm)	185	3618	1389
<u>Condition of Treatment</u>			
Aeration (Hrs.) day	-	-	24
Aeration Rate (Cu.Cm./Min.)	-	-	1400
Retention Time (Hrs.)	13	32	22
<u>Effectiveness of Treatment</u>			
pH	8.1	8.8	8.4
Phenol Removal (%)	71	100	91
C.O.D. " (%)	70	100	84

Mills

METHODS ADOPTED BY IMPERIAL OIL LIMITED TO PREVENT
PHENOL CONTAMINATION OF THE ST. CLAIR RIVER IN THE
EVENT OF AN ACCIDENT

By

J. T. Williams

Imperial Oil Limited

Sarnia, Ontario

Imperial Oil's Sarnia Refinery located on the upper St. Clair River must, of necessity, maintain close watch on the quality of its effluent waters. Seventy miles down-river lie the cities of Detroit and Windsor which use the St. Clair for industrial and domestic water supply. There are also several smaller communities downstream of Sarnia making similar use of the river. Phenol which is used in a treating plant and also produced in various refining processes could cause a serious pollution problem if allowed to escape in large quantities in the effluent waters. Over the past four years Sarnia Refinery has spent a considerable sum in reducing the phenol content of its effluent. To provide some background to the present status it is necessary to review the phenol picture from 1952 to date.

In 1952 the phenol treating plant which is employed in the finishing of lubricating oils was the chief source of phenol contamination. As early as 1951 consideration had been given to the construction of some type of Biological Oxidation Plant. It was discovered by systematic research and checking of the plant that a large amount of phenol to the river was being contributed by leakage from underground lines. As a result all phenol carrying lines were raised above ground and the plant area paved with asphalt. Several drainage sewers in the plant proper were diverted so as to discharge to a phenolic water sump. This sump was very carefully watched for phenolic content and at such times as this became too high to be discharged to the sewers it was pumped to a phenolic water tank. By 1953 the foregoing steps had reduced the phenol discharge of this plant from 200 - 300 pounds per day down to 50.

At this time, however, the new Catalytic Cracking Unit went into operation and this unit, alone, contributed about 400 pounds per day of phenol. This material, along with phenolic water from the Central Treating Plant, was eventually processed through a sour water stripper which removed a certain percentage of phenols and also stripped it of hydrogen sulphide. The effluent was then discharged to the Biological Oxidation Plant for final phenol removal.

The phenolic effluent from the Phenol Plant proper was also pumped to the Biological Plant. The actual successful operation of the Biological Plant did not occur until December of 1954.

Phenol control was maintained during 1955 at the required level until December 13 when a tube in one of the exchangers at the Phenol Plant split open. This resulted in a fairly high loss of phenol to the river before measures could be taken to bring it under control.

At a Refinery Management meeting immediately called it was decided that a change in policy was necessary. In spite of all normal precautions and the elaborate system installed during the past few years to collect and destroy phenol from all known sources, it was apparent that equipment drainage, line breaks, etc., even if infrequent, were unavoidable. The only solution, therefore, was a complete isolation of the Phenol Plant area from the Refinery sewer systems.

As shown on Slide 1, surface drainage including leaks, drips and washings are collected by the oily water sewer system which empties into a sump. Drainage from the tank area also goes to the sump via an 18" sewer and the normal flow in this sewer is prevented from flowing to the separators by a weir in catch basin "A". An existing steam sump pump is being replaced by a motor-driven deep well type to give increased capacity. This will prevent overflowing of the weir during normal rainfall, but does not allow for flash floods.

The clean water sewer flow is made up from overflow of the tempered water tank No. 1058, flow from a box cooler and three tube coolers not using tempered water. Tempered water circulates through seven overhead condensers and two coolers to the tempered water tank and return. 1100 GPM make-up maintains this water at 60°F. during the winter. In the summer 2000 GPM are required, and in both cases the overflow is too great for the Bio Plant to handle. It was essential that this cooling water system be isolated from the Refinery sewers.

The Bio Plant is another source of pollution due to the possibility of leaks or overflow from the storage tanks and vessels which would drain to No. 11 Separator. This would also include a new 25,000 barrel emergency storage tank.

RECENT STEPS TAKEN TO ISOLATE THE OILY WATER SYSTEM

To date, the following steps have been taken to isolate the system:

- (1) The discharge from the phenol feed preheater C629 was diverted to the oily sewer.
- (2) The sewer connection from the sump to catch basin "A" blocked off to prevent any flow to 9 and 10 Separators.
- (3) The natural reservoir is formed by the tank lot, which is $2\frac{1}{2}$ feet below grade.
- (4) A motor driven pump was set up to take suction on catch basin "E" and pump any collected water to 912 tank, which was set aside as temporary emergency storage.
- (5) Other catch basins were isolated from the Phenol Plant sewer as shown on Slide 1.
- (6) Process men were employed on shift to sample and test the effluent from the cooling water system at half hour intervals. If the phenol content rises above 5000 parts per billion, if necessary the Plant could be shut down.

PROPOSED FACILITIES

Isolation of Oily Water System

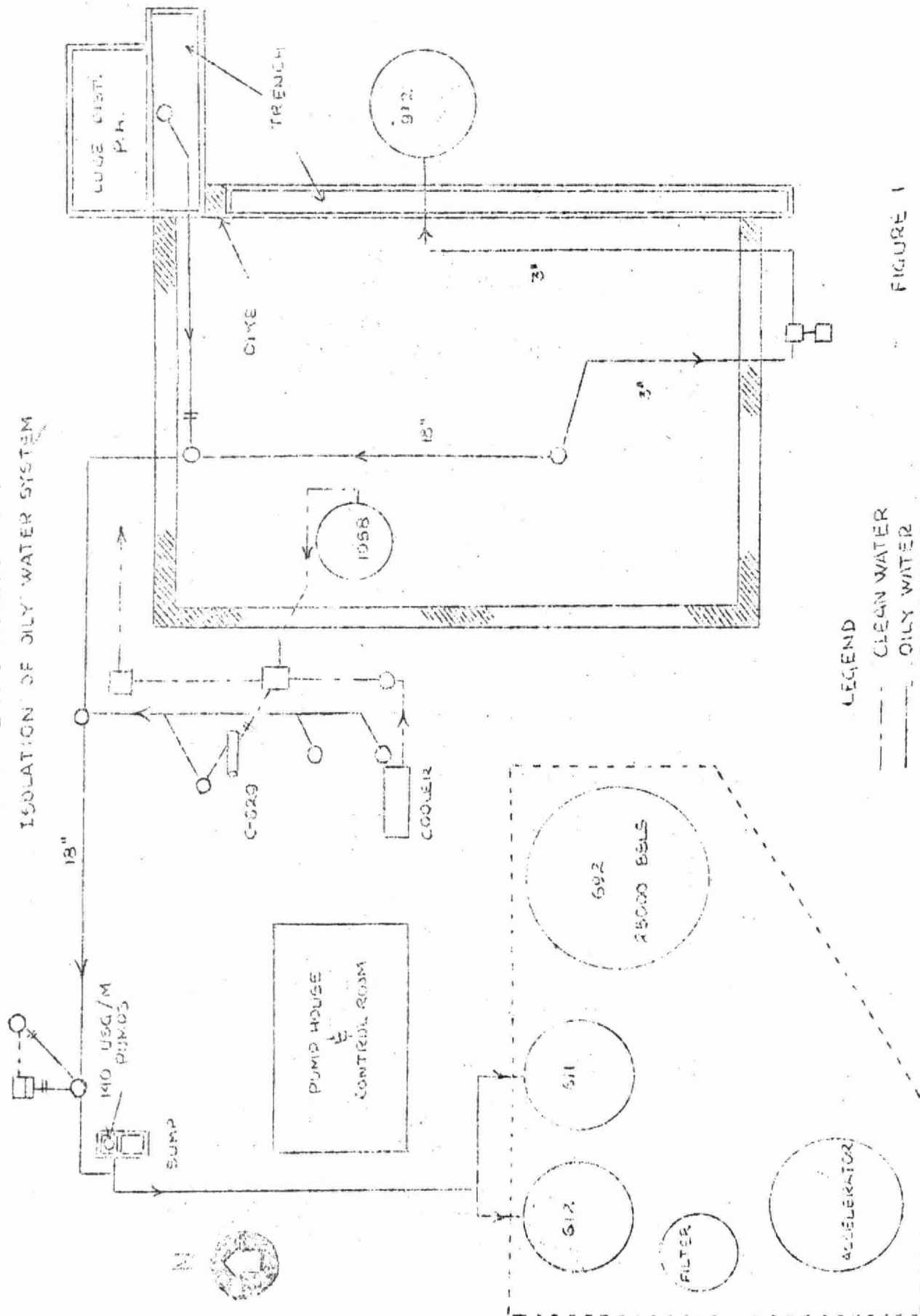
The following steps have been proposed and will be carried out to completely isolate the oily water system.

- (1) The installation of a spare deep well pump to be located in the sump. This will ensure continual operation in the event of a pump failure.
- (2) The erection of a new 25,000 barrel tank to supply surge capacity for the Biological Plant. This tank will be located as shown in the vicinity of the foregoing Plant, and the entire area will be enclosed by a concrete retaining wall. (Figure 1)

Isolation of Clean Water System

- (1) The installation of a cooling tower which will supply 78°F. water to the overhead condensers and existing coolers now using service water.
- (2) Three motor-driven deep well centrifugal pumps, each having a capacity of 1750 GPM at 85 psig, to take suction on the cooling tower and supply water to the Phenol Plant.

PHENOL PLANT ISOLATION OF OILY WATER SYSTEM



LEGEND
 --- CLEAN WATER
 --- OILY WATER
 --- PROPOSED

FIGURE 1

- (3) 12" supply and return lines as shown on Figure 2.
- (4) A 150 GPM motor-driven centrifugal pump to return water from the open cooler box to the 12" return line. This pump will be placed on level control.
- (5) Make-up water to be supplied from an existing 8" main, and purge lines as shown to be connected to the Biological Plant and No. 12 Separator.
- (6) A continuous phenol analyzer to be installed on the blowdown line from the cooling tower and to actuate an alarm in the Phenol Plant control room when the phenol content reaches a predetermined level.

The foregoing system will completely enclose both the oily and clean water system and should prevent any possibility of phenol escaping to the river from this Plant.

We feel confident that following the installation of the foregoing facilities, Imperial Oil's Sarnia Refinery will be able to meet and maintain the I.J.C.'s objective for phenol content in the St. Clair River. These facilities have been designed to meet practically any eventualities which might arise. Slide No. 3 indicates the extent of Imperial's efforts to reduce phenol contamination since 1950 and the target for 1956.

PHENOL PLANT COOLING TOWER INSTALLATION

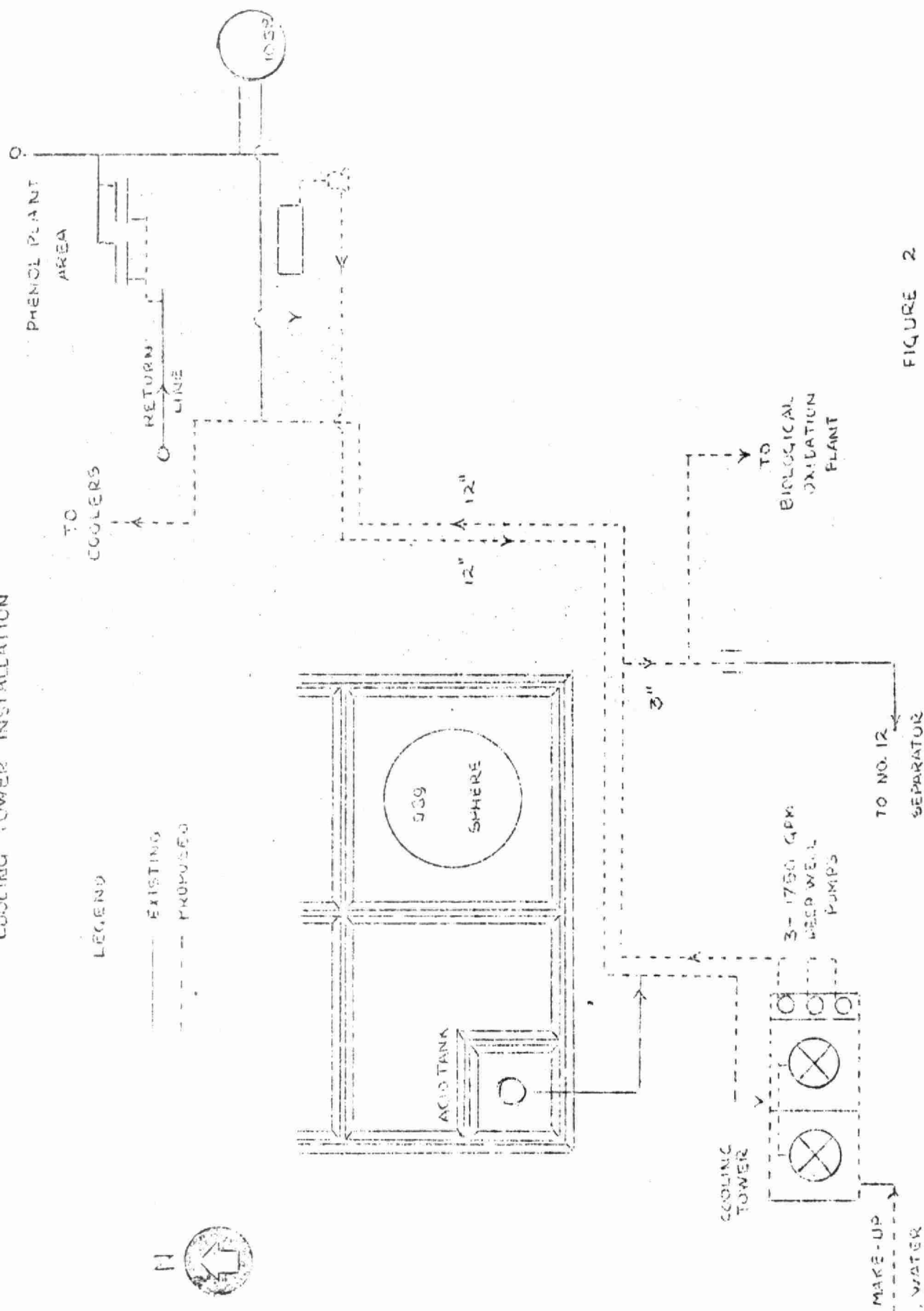


FIGURE 2

THE USE OF BIO-ASSAYS IN RELATION TO THE
DISPOSAL OF TOXIC WASTES

By

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Public Health Service

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Although bio-assays are only now coming into general use for evaluating the toxicity of water pollutants, the technique is neither new nor untried. Bio-assays have been used for meeting a variety of problems for many years. Perhaps one of the earliest uses was the employment of food tasters by persons of high rank to determine if the food was safe to eat. This use of humans as bio-reagents was simple but evidently effective and was practiced over wide areas for a considerable period. In more recent times the bio-assay technique has been effectively used for the assay of drugs, toxins, antitoxins, vaccines, insecticides, vitamins, and many other products.

Bio-assays to determine the toxicity of certain wastes to fishes were used in Europe about fifty years ago. In this country pioneering work has been done by Shelford, Belding, Carpenter, and Ellis in the development of methods and procedures. Hart, Doudoroff, and Greenbank developed a method of approach for obtaining comparable data. In an effort to standardize bio-assay methods they evolved relatively simple procedures which yield results applicable to most practical problems. They summarized pertinent information on bio-assays in a comprehensive book (1). Since this work has been out of print for several years and only a small number were printed, it is generally unavailable. It has now been superseded by a more recent publication entitled, "Bio-assay Methods for the Evaluation of Acute Toxicity of Industrial Wastes to Fish," which appeared in the November 1951 issue of Sewage and Industrial Wastes (2). This publication was prepared by Section III of the Subcommittee on Toxicity of the Federation of Sewage and Industrial Wastes Associations which was under the chairmanship of Dr. Peter Doudoroff.

The bio-assay is a procedure for determining the toxicity of a material or mixture of materials to selected organisms under specific conditions. By varying the

type of dilution water, bio-assays may be used to determine how the toxicity of a particular material or substance is influenced by certain water quality characteristics. They may be used in like manner to determine the toxicity of such materials or wastes to particular species or groups of organisms.

In bio-assays to determine the effectiveness of insecticides for the control of certain insects, results are expressed as LD_{50} , that is, the dose which is lethal to half of the insects. In fish toxicity investigations, results are reported as the 24-, 48-, or 96-hour median tolerance limit (TL_m); that is the concentration of the waste which kills half the test fish in 24, 48, or 96 hours. Several bio-assay methods may be used in determining the TL_m values of a waste, the method used being determined by the character of the waste. For many wastes the simple static bio-assay may be used. This test is made by preparing serial dilutions of the waste in a logarithmic series of concentration such as 10, 5.6, 3.2, 1.8, and 1 percent of the waste, in water from the receiving stream or a prepared water similar to the stream water; placing fishes in these various dilutions and recording kills at 24, 48, and 96 hours. The observed mortality at 24, 48, and 96 hours in the different concentrations are plotted on semi-log paper, the percent survival of fish on the arithmetic scale, and the concentration on the log scale. The TL_m values are then obtained by means of straight line graphical interpolation reading the TL_m directly from the graph where the line crosses the 50 percent survival line.

For wastes of completely unknown toxicity, it is desirable to make simple exploratory tests over a wide range of dilutions of the waste such as 10, 1, and 0.1 percent. These tests can be made in wide-mouth one-gallon glass jars using two liters of the test solution and two fish. Such screening tests indicate the range of dilutions which should be used in the full scale tests.

Some wastes require special treatment because they may be complexed, precipitated, oxidized, influenced by the waste products from the fish, or may be volatile and/or have great oxygen demand. Many of these problems may be met by renewing the static solutions at regular intervals. If the toxicant is volatile and/or has a large oxygen demand, the Doudoroff method (2) of bubbling air or oxygen through the test solution can be used to maintain D.O. with a minimum loss of volatile components. For wastes presenting these problems a constant flow procedure where the pollutant and the dilution water are constantly renewed may be necessary. However, this method requires considerable equipment and large volumes of effluent and dilution water. Static bio-assays are adequate for many wastes.

The bio-assay is a tool which can prove very useful for the detection and evaluation of certain types of pollution problems. It provides a direct approach to the problem of the toxicity of wastes to aquatic life and in most instances it is also the quickest and most economical approach. It provides information on the toxicity to fishes of a particular waste in a particular receiving water. Such toxicological information is basic for the establishment of water quality criteria for aquatic life.

Many have observed that the toxicity of the same or similar wastes may vary widely in different streams. There are many factors which may influence the toxicity of a waste or material. Among these are temperature; dissolved oxygen and CO_2 ; pH, alkalinity, and hardness; and wastes or other materials already in the receiving water. In general, materials are more toxic at higher temperatures and at low dissolved oxygen levels. Alkalinity and hardness are of outstanding importance in determining the toxicity of the heavy metals through precipitation, complexation, or buffering action. Even small changes in pH can greatly alter the toxicity of such materials as ammonia, the metals, metallo-cyanide complexes, and some of the weak acids. Carbon dioxide may, through its effects on pH render some materials more toxic or it may serve to make others less toxic. Another outstanding variable is the synergistic or antagonistic effects of materials naturally present and of wastes which have been added upstream.

Cyanide has been shown to be more toxic at low dissolved oxygen levels and it has also been found to be more toxic at higher temperatures. The heavy metals are considerably more toxic at the lower pH levels as they are more soluble in acid solutions. Ammonia becomes very rapidly more toxic as the pH increases above 8.0. This is probably because the NH_4OH molecule is much more toxic than the NH_3 ion. Being a weak base ionization of NH_4OH is depressed as the pH increases with the result that more and more molecules are present as the pH raises and thus the toxicity increases. Ellis (3) found that the toxicity of ammonia increased 200 percent or more between pH 7.4 and pH 8.0. Acid salts of ammonia can be expected to be less toxic in soft water with lower buffering capacity as they lower the pH and decrease the concentration of NH_4OH molecules. The base is much more harmful than ammonium salts in the same water and its toxicity can be reduced or eliminated by the addition of acid. Thus the total amount of ammonium ion present as indicated by chemical analysis is not necessarily a measure of toxicity.

Some cyanide compounds are very toxic but some others are relatively nontoxic. Ferrocyanide and ferricyanide were at one time considered relatively nontoxic as fish lived for short periods in concentrations of 1000 to 2000 p.p.m. of these materials with no apparent harm. However, when exposed to sunlight these materials are subject

to photo-decomposition with the result they break down and become toxic at concentrations as low as 2 p.p.m. (4). The toxicity of many of the metal-cyanide complexes is greatly influenced by pH. Doudoroff (5) has reported that fish can withstand more than 1000 times as much nickel cyanide complex at pH 8 as at pH 6.5. He also found that the doubling of the hydrogen ion concentration, that is, the reduction of the pH 0.3 unit from 7.8 to 7.5, can result in more than a tenfold increase in the toxicity of a NaCN-NiSO₄ mixture. From these findings it is quite apparent that the concentration of cyanide reported in an undiluted cyanide bearing waste is not necessarily a reliable measure of the toxicity of the waste in the receiving stream.

The total alkalinity and hardness of a receiving water are factors which influence the toxicity of a waste. In studies carried on at the Robert A. Taft Sanitary Engineering Center in Cincinnati, it has been found that many of the metals are much more toxic in soft water than they are in hard water. For example, Beryllium and Uranium were 60 to 80 times more toxic to fathead minnows in soft water than they were in hard water. Copper has killed fish at concentrations as low as 0.06 p.p.m. in soft water with a low pH; whereas it is well known that during algicidal operations in some lakes concentrations well above 0.5 p.p.m. have been applied without lethal effects to fishes. The toxicity of solutions containing Titanium, Vanadium, Zirconium, and other metals may be reduced due to precipitation or complexing with materials present in the water, thus reducing the amount of metal ion in solution.

Dissociation, recombination, and oxidization are also of importance in determining the toxicity of a waste in a receiving stream. Recent studies at the Sanitary Engineering Center disclosed that fish lived longer in a relatively high concentration of Na₂S than they did in weak solutions. In the weaker solutions oxidation produced SO₄ which, due to dissociation and recombination, caused a lowering of the pH. This in turn increased the amount of H₂S formed by the dissociation of Na₂S. Since it is the H₂S molecule which is largely if not entirely responsible for the toxicity, the lowering of the pH depresses the ionization of the H₂S and the toxicity increases.

Moderate concentrations of metal salts such as those of sodium, magnesium, potassium, or calcium which are harmless to fish in sea water and highly mineralized fresh water can be injurious when they occur alone or in physiologically unbalanced solution. The toxicity of copper, zinc, and other heavy metals is counteracted by calcium and other antagonistic metal cations. On the other hand copper and zinc, copper and cadmium, and zinc and nickel are strongly synergistic. In studies carried out at the Center, Doudoroff found that 0.025 p.p.m. of copper with 1 p.p.m. zinc in soft water were more toxic to fathead minnows than 0.2 p.p.m. copper, or 8.0 p.p.m. of zinc alone.

It is evident from the foregoing that the character of the receiving water can cause wide variations in the toxicity of many materials to fishes. Further, wastes already in a stream or added subsequently may influence the toxicity of another waste through antagonistic or synergistic action. Chemical analyses alone cannot indicate toxicity in most instances but a knowledge of the chemical makeup of a waste can be very helpful in a number of ways when the toxicity is determined by bio-assay. Further, analytical methods are not available for all substances which may be toxic to fishes and methods are not sensitive enough to detect some materials at the low concentrations at which they are toxic to fish. In addition, a knowledge of the main constituents of a waste and their individual toxicity would not necessarily provide an indication of the toxicity of the complex waste or its variation with changes in water quality.

In view of this situation it is believed that water quality criteria expressed in general numerical terms cannot be set up for all materials to apply over extensive areas or even to all parts of the same stream. If such a cook book approach is used, permissible levels must be set so low that the allowable concentration is safe even under those situations in which the material is most toxic. It is apparent, therefore, that rigid standards applied over wide areas will penalize those industries on streams having water in which the wastes are less toxic as the criteria must be set at a level to protect aquatic life in those streams having water quality characteristics under which the waste is most toxic.

It is believed that there are three main criteria which can be assigned numerical values which are applicable over extensive areas. These are criteria for temperature, D.O., and pH. While there are some substances the toxicity of which is not significantly affected by water quality, it is believed that from the standpoint of fairness and economy it is desirable to adopt the tailor-made approach for toxicity criteria and establish safe levels based on the amount of a particular waste that can be added to a particular stream at a specific point without detriment to aquatic life. This can best be determined by means of bio-assays made with the waste in question and using for dilution, water from the receiving stream and employing local fish as bio-reagents. The bio-assay takes into consideration most of the factors governing toxicity and is a direct approach to the problem.

Bio-assays are a tool which can be used by industry and enforcement agencies. They can be used by industry to answer a number of questions: (1) Is the waste toxic to fishes; (2) How toxic is it; (3) If it is so toxic that fish will be killed during low flow periods, can the wastes be stored and released according to stream flow so that critical concentrations are not attained; (4) If water is not available

to provide needed dilution, how much must the toxicity be reduced; (5) How effective are the various treatment methods for the reduction of toxicity; and (6) How does the toxicity of the effluent vary. Continuous flow bio-assays set up as a monitoring system can be used to detect any unusual toxicity due to spills or the release of wastes from certain processes during short periods. By means of the proper sampling of waste flows and the use of bio-assays, the main sources of toxic wastes in a plant can be located. If the toxicity of a total effluent is attributable to the waste from one or more unit processes, wastes from which are small in volume, it is evident that bio-assays can be of value in reducing waste treatment cost as it is much cheaper to dispose of or treat a small volume of waste than it is to treat the entire waste of the plant.

Bio-assays can be helpful to pollution control agencies in determining if a particular plant should be located on a given stream. Bio-assay of wastes from pilot plants or similar existing plants, using for dilution, water taken from the receiving stream at the point where it is proposed to discharge the waste, will indicate the toxicity of the waste in that particular stream, the amount of dilution water required, and the advisability of locating the industry at that point. Bio-assays can also be used to determine: industries contributing toxic wastes; the relative toxicity of different effluents and the total wastes from different plants; and the ability of a stream to assimilate the wastes of an industrial complex. They will, in addition, be of value in apportioning stream use equitably among the various industries according to the toxicity of their total waste and for detecting violations of regulations. As industry increases and water for dilution becomes more critical a knowledge of the total and relative toxicity of the wastes of different industries will be basic to fair and correct handling of waste treatment and discharge. The time may come when industries will be located according to the character of their wastes. It certainly would be logical to think of waste disposal before the plant is located, to locate only where there is sufficient dilution water, and to group industries in such arrangement that their wastes are antagonistic rather than synergistic. The disposal and treatment problems of an industry having considerable ammonia in its waste, and located on a stream high in acid mine waste, would certainly be complicated by the location of another plant upstream which had an alkaline waste that raised the pH of the stream above 8.0, because even slight increases in pH above this level bring about great increases in the toxicity of ammonia. The waste disposal problem of a plant located on a hard water stream and having heavy metals in its waste might well be increased by establishment upstream of a plant discharging sufficient acid to lower the pH of the stream as the heavy metals are more toxic at lower pH. The release of materials which are synergistic to existing wastes in the stream can also create problems.

As now commonly used, bio-assays determine acute toxicity or direct injury to fish upon short exposure. They do not take into consideration the long time or chronic effect or the possible injury to aquatic life other than the test fish. The TL_m values, since they indicate concentrations at which half the fish are killed, obviously do not represent concentrations which are harmless in fish habitats. Liberal application or dilution factors must be applied to indicate safe disposal rates. Considerable research will be required to determine application factors for the various industrial wastes. It is expected that the application factor will be a value which, when used with the TL_m , will indicate the dilution needed for that waste in order to render it safe for aquatic life.

There are several factors which necessitate that dilutions essential for the protection of aquatic life be several times greater than the TL_m value at which only half the fish survive. In the first place it is required that all fish survive not for just 48 hours but under conditions of continuous exposure. Further, other fish may be considerably more sensitive than the test fish. Fry and other life history stages are generally more sensitive than adult fish. It is known that many fish food organisms are less resistant to certain toxicants than are fish. Conditions should be favorable not only for fish but for fish food organisms if the former are to grow, reproduce, and provide a suitable crop. In addition, some allowance must be made for variations in the volume and toxicity of effluents. Maximum toxic conditions are the limiting factor which must be provided for in the protection of aquatic life. Changes in water quality characteristics, synergism and antagonism between toxicants, and natural purification are other factors that must be kept in mind. When all these factors are considered it is apparent that the dilution required for the protection of aquatic life may well be 5 to 10 times that of the 48 hour TL_m .

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TOXICITY OF CYANIDES TO FISH

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Cyanide is a chemical which has been known to mankind for a long time. In years past, it was the favourite poison for hastening the accession to the thrones of Europe. As a safeguard, the royal families employed tasters to assure that the food was not poisoned. Cyanide is today one of industry's favourite poisons for killing fish, and again the taster principle, in the form of the bio-assay, is used to determine the safety of water for fish.

Cyanide is an important chemical, especially to the metal industry. Its power to form soluble complexes with heavy metals makes it very useful in plating and in the refining of gold and other metals. It is also commonly discharged as a waste from coal gas production, and as a by-product of coke ovens.

The striking effect of even small quantities of cyanide in water in killing fish has stimulated biologists and chemists in Canada, the United States and Britain to conduct investigations to determine just how much cyanide is required to kill fish. Unfortunately, much of the information that appears in the literature is based on batch tests where fish were simply put in solutions of known concentrations and the time-to-death determined. It has since been shown that the concentration of cyanide drops rapidly in the solution because of absorption on the mucous membrane, and if the solution is aerated to maintain favourable oxygen levels, much of the cyanide is lost as volatile hydrocyanic acid. Thus, if the fish do not die within a relatively short time, the concentration is soon lowered to a point where they are able to live indefinitely. For this reason, tolerable limits have often been set too high, or at least on the basis of incomplete information.

Ontario is fortunate and proud of the valuable species of fish that inhabit its streams and lakes. In many cases, these fish, belong to the Salmonoid or trout-herring family which are known to be some of the forms most susceptible to cyanide and other toxicants. As only incomplete information was available on the effect of cyanide to native fish, an experiment was planned so that the dangers of cyanide pollution could be assessed on a scientific basis and thus provide better information for industry.

For the purpose of this experiment, four-inch speckled trout were used as a test fish. They were acclimated to the temperature used in the tests for a period of at least two weeks, and during acclimation and testing were kept under favourable oxygen conditions. The apparatus built provided a continuous flow of a liter and a half a minute of solution bearing a known concentration of potassium cyanide. For each concentration tested, ten trout were used. Each fish was removed from the test solution when it failed to maintain its balance and was not responsive to stimuli. Because of the time available, a limit of 5000 minutes,

about three and a half days, was set as the end point of the series.

The test fish were subjected to concentrations of from 2 ppm to 0.08 ppm. While cyanide concentrations are expressed as the CN ion, the most toxic form is considered to be the HCN molecule. At concentrations of 2 ppm, the time-to-overturn was approximately five minutes. As the concentrations were reduced to 0.5 ppm, little change was noted in the time-to-overturn. This is undoubtedly due to some minimum time required for a fish to die and is not dependent upon the cyanide concentration. At about this point the character of the slope changes and enters a straight line logarithmic phase where the log of the geometric mean of time-to-overturn is proportional to the log of the cyanide concentration. At a concentration of .2 ppm, the fish overturned in 150 minutes and at .1 ppm, the overturn occurred at about 1400 minutes, or approximately one day. The final cyanide run used was .08 ppm, where half the fish in two tests had overturned within 5000 minutes, three and a half days. This final point is a little off the curve, but within the limits of experimental error.

The experiments were ended at this point because of the time available and not because it was considered the limit of toxicity. Fish that had been subjected to such low concentrations as .08 ppm - which is less than 13 ounces of cyanide in one million gallons of water - soon showed signs of distress. Their movements became sluggish and they appeared to release gas from the air bladder, so that they remained on the bottom. Periodically, exaggerated activity would occur when one or more fish would suddenly circle the chamber and jump for a short interval, then drop back to the bottom, apparently exhausted and often unable to maintain balance for a short period. At low concentrations, the trout soon began to take on a dark colour, which easily distinguished them from other fish if returned to the holding tank.

Both the behaviour effect and the colour change indicate that even in these low concentrations, cyanide soon affects the fish and would put them in a very unfavourable position under natural conditions.

A similar experiment was performed by two English authors using rainbow trout. Again the fish were kept in favourable conditions, but at a higher temperature (17.5°C.). Their results are quite similar to the results of the experiment just described, although the speckled trout died more quickly at the higher concentrations.

Cyanides generally enter the water as industrial effluents often from the plating industry. In plating, they are in contact with various metals such as iron, nickel and zinc. Being highly reactive, the cyanide is generally complexed in some form or other. Realizing this, a number of toxicity studies have been designed to test the lethal limits of these complexes. The literature contains neat figures which indicates that relatively high concentrations of ferrocyanides, such as 2000 ppm, are not toxic to minnows and goldfish, or that 8000 ppm is not toxic to trout in one hour. The complexing of cyanide with nickel salts has recently been suggested as a method of stabilizing cyanides in order that they may be safely discharged. Unfortunately, many of these data have been published from short-term experiments and with little regard for a number of chemical and environmental factors that

may profoundly alter the toxicity.

A few years ago in the State of New York, several serious fish kills occurred in rivers receiving plating wastes. The toxic material undoubtedly came from these industries, but the cyanides were known to be complexed with iron. While this complex had a high threshold toxicity, still fish were dying at low concentrations. An investigation into the cause of these mortalities showed that under the influence of strong sunlight, the iron cyanide complex was broken down and that the free CN ion was released. It was demonstrated that photo decomposition of concentrations as low as 3 ppm of ferro- or ferricyanides was lethal to minnows, a very different figure from the 8000 ppm previously quoted as not killing trout.

Many metals complex readily with cyanide, even in dilute solutions. Nickel cyanide is such a complex and it is known to be relatively stable. The paper published suggesting the addition of nickel salts as a method of treating cyanide wastes included results of a short bioassay, and the evidence appeared rather convincing. The United States Public Health Service under Dr. Tarzwell's direction has recently conducted an extensive study of the toxicity of various complex cyanides, including an investigation of this nickel complex. Their findings have shown that relatively high concentrations of about 100 ppm can be tolerated with no evident harm to fish, providing the water is alkaline, but the toxicity threshold drops very rapidly as the pH decreases. It was shown that if the pH dropped from 8.0 to 6.5, the toxicity of this complex would be increased a thousandfold.

Zinc and cyanide form a complex which is almost completely dissociated in dilute solution. It would be expected that fish would succumb to either the zinc or the cyanide ion, depending upon which was present in lethal concentrations. Experimental work has shown that a synergetic action occurs when both are present, and mortality occurs at a level below that found for either cyanide or zinc.

One other case of a cyanide association which is more toxic than cyanide by itself was demonstrated when effluents containing liquor from coal gas manufacturers were chlorinated. This effluent was found to be very toxic and yet the fish were found to survive in unchlorinated effluent. It was later demonstrated that where chlorine was applied in quantities insufficient to oxidize the CN ion, cyanogen chloride was formed which was more toxic than the cyanide alone.

Earlier in discussing the experiment on the effects of cyanide on speckled trout, it was mentioned that the experiment was carried out under favourable environmental conditions. In this case, a continuous flow of water at 10°C. was supplied which was nearly saturated with oxygen. In many cases, a stream receiving a cyanide pollutant may not be such a favourable environment, and undoubtedly the toxicity of the waste will be increased under these conditions.

The environment may influence toxicity in two ways. Firstly, the chemical nature of the water may affect toxicity in a purely chemical fashion, i.e. by increased dissociation of complexes at low pH's or by reducing the toxicity at least temporarily by the formation of stable

complexes with substances present in the water. This purely chemical influence has been more or less covered already in the discussion of complex cyanides. The second way in which the environment may influence toxicity is a direct physiological effect on the fish which may put it in a position where it is unable to withstand cyanide concentrations or compete in an environment where it might otherwise survive.

While no person is sure of the exact effect of the cyanide, it is known to inhibit almost any enzyme processes within the body cells. Undoubtedly, cyanide is transported by the blood throughout the body and the actual death is caused when the first essential function is inhibited. This is thought to occur in the nervous system. Fish are cold-blooded and the metabolic rate is determined by the temperature of its environment. Thus if the experiments had been maintained at 20° instead of 10°, the metabolic rate would have been considerably increased, and death would have occurred faster.

A second important environmental factor is the oxygen concentration in the water. Evidence from work done in England on rainbow trout shows that the time-to-overturn at 30% oxygen saturation in 8°C. water is 12 minutes, whereas in water 80% saturated fish will live 100 minutes.

It should be noted that a relationship occurs between the temperature and the dissolved oxygen which put a double stress on the fish, as at high temperature, not only does the metabolism increase, but the concentration of oxygen at saturation is considerably lowered.

Several additional factors have been shown to be important in laboratory studies and undoubtedly are important in the resistance of fish under natural conditions. The size of fish used in laboratory studies must be similar to obtain reproduceable results. In general, small young fish are better able to withstand adverse conditions, although little is known of the effects of toxic material to eggs or young fry. Feeding has been shown to affect results and generally fish are not fed 24 to 48 hours before being subjected to tests. The general health of fish is also important as fish living in an unfavourable polluted environment may succumb when healthy population would survive or perhaps have the stamina to move and escape the pollutant.

The resistance of various species of fishes to cyanides or other toxic material is a subject on which there is little information. The literature contains a number of references to the effects of cyanides on several species, but the methods used are often not comparable and the chemical composition of the dilution water used, which is of prime importance, is often unpublished. Certain species have been considered hardy and others susceptible to toxicants, but as more information becomes available, it is apparent that a fish thought to be hardy may be resistant to one poison and susceptible to another.

It was mentioned earlier that the foregoing study was begun in order that the dangers of cyanide poisoning could be assessed on a rational basis designed to meet conditions found in Ontario.

The Pollution Control Board in their "Objectives for Water

Quality for the Province of Ontario", have included cyanides under the classification of "highly toxic wastes" and require that they be eliminated from effluents. At present cyanides are not determined easily or with accuracy below about 0.5 ppm. Thus the word "eliminate" requires that they be below the level of analysis. Ontario has not set arbitrary permissible limits on any form of pollution. Water, like any other natural resource, should be used for the good of all, but not wasted with careless and unnecessary pollution. If arbitrary standards were set on the basis of the preceding experiments, a limit of about 0.02 ppm would have to be set in the receiving water. This is rather ridiculous as there is no means of analysis which will give a significant figure at this level. In doing the cyanide experiments, fish were found to give better accuracy at low concentrations than chemical analyses. No differentiation is made for complex cyanides. They have been shown to be unstable under a number of physical and environmental conditions, and at the present state of knowledge must be regarded as a potential source of cyanide.

If there is any question as to whether a cyanide waste with all its complicated reactions can be safely discharged, a bio-assay should be made. The information required in any waste-disposal problem is: will this waste harm the stream, and what is the safety factor in dilution that must be maintained? A bio-assay will readily supply this without the necessity of a long series of difficult analyses and a literature search for the interpretation of the results. The chemist will take readily to this job, as it is a common biological observation that most chemists are really biologists at heart.

AIR POLLUTION LEGISLATION IN GREAT BRITAIN

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There is little merit in detailing the exact provisions of the British Legislation relating to air pollution control without considering the effectiveness of the laws in dealing with the British problem. This paper, therefore, will deal with the British approach in a general way and then discuss the contribution of this approach to the control of pollution in Britain.

First, it must be appreciated that atmospheric contamination is not one problem, but a series of problems varying from the very simple, through to the difficult, and to the near impossible. Second, it must be realised that though some problems are near impossibles, a consideration of the problems involved in the handling of radio-active materials, especially the handling of the large quantities involved in the manufacture of nuclear bombs, will show that almost any problem can be solved if we are prepared to spend enough on it. The degree of control exercised depends almost entirely on economic considerations.

Among the more easily controlled pollutants is smoke, and since smoke is the traditional pollutant of the older civilizations which depend on coal (especially high volatile bituminous coal) for heat and power, smoke control laws (Smoke Abatement laws) are by far the most common air pollution control laws. In the U.S.A., which is the only country besides Britain to have made any serious attempt at pollution control, most of the laws refer exclusively to smoke control. This is due partly to the lack of technical knowledge which precludes the legal definition of firm limits to allowable pollution for pollutants other than smoke and partly due to the inability of the medium and small towns to finance the skilled staff and special equipment necessary to effect complete control of the pollutants other than dust and smoke.

Herein, we feel, lies the weakness of the U.S. system with its insistence on control at the municipal rather than state or federal level.

It must be appreciated that the control of all pollution in Great Britain is covered by the Common Law relating to nuisance. All the subsequent laws are merely devices to assist in the interpretation of this basic law. The word nuisance has a wide range of meanings and in order to avoid the confusion which would exist due to variations in interpretation, additional laws have been passed declaring that if certain things are done or certain states exist, a statutory nuisance exists without the need for anyone to prove the existence of a nuisance within the meaning of the Common Law. One of the earliest laws referring to smoke pollution is the law passed during the reign of Elizabeth I, prohibiting the use of coal within the city of London while Parliament was in session. Elizabeth I must have felt more competent than Queen Eleanor who just about 700 years ago moved the court from London

to Nottingham to escape "London's insufferable smoke". In 1662, John Evelyn wrote his celebrated pamphlet "Fumifugium" (1) in which he made the first plea for zoning, to wit, a plea to His Majesty to order all brewers and others who produce smoke to move their factories outside the city. Many an industrialist has done just that, only to find the city grow towards him and in a short while engulf him once more. Zoning is a widely accepted practice, but no-one has yet prohibited dwelling houses in industrial zones. At the present time smoke emission is controlled by The Public Health Act of 1936. It is not necessary to consider this Act in detail since it has not proved to be very effective in dealing with the smoke problem in Britain and it is almost certain to be superseded by new legislation at present before Parliament which will be known as the Clean Air Bill.

The Public Health Act, 1936, constitutes as statutory nuisances any installation for the combustion of fuel which is used in any manufacturing or trade process and which does not so far as practicable prevent the emission of smoke; and any chimney (except a chimney of a private house) emitting smoke in such quantity as to be a nuisance. Where a notice is served by a local authority requiring the abatement of a nuisance is not complied with, proceedings may be taken before a court of summary jurisdiction. The court can impose a fine of up to Fifty Pounds Sterling and may make an order for the abatement, or prohibition of recurrence, of the nuisance.

It is, however, a defence in any proceedings for discharging smoke, other than black smoke, to show that the best practicable means for preventing the nuisance have been used. "Best practicable means" refers both to the provision and maintenance of adequate plant and to the manner in which the plant is used.

The expression "smoke" is defined in the Public Health Act, 1936, as including "soot, ash, grit or gritty particles".

The Acts contain a saving clause for certain industrial processes. The provisions of the Acts may not be applied so as to obstruct or interfere with the working of mines or with a number of operations in iron and steel works.

Under The Public Health Act, 1936, local authorities may make by-laws, subject to confirmation by the Minister of Housing and Local Government, regulating the emission of smoke of such colour, density, or content, as may be prescribed by the bye-laws. Such bye-laws do not apply to private houses. The bye-laws usually make it an offence to discharge black smoke for two minutes in the aggregate within a continuous period of thirty minutes. 229 local authorities in England have so far made such bye-laws, all of them dealing only with black smoke.

The Public Health Act, 1936, also constitutes as a statutory nuisance any dust or effluvia caused by any trade, business, manufacture, or process and which is injurious or dangerous to the health of, or a nuisance to, the inhabitants of the neighbourhood.

There is again a "best practicable means of prevention" defence. (2)

The important point to note here is that the above act is to be administered by the local authority at the municipal level, and that it represents the total responsibility of the local authority.

Railway locomotives are required by the Railway Clauses Consolidation Act, 1845, to be constructed on the principle of consuming their own smoke and it is an offence for any locomotive to fail to do so. No particular body, however, is charged with the duty of enforcing these Acts, and any person or corporate body may complain to the courts.

Motor vehicles are required by an Act passed in 1951 to be constructed, maintained and operated in a manner to prevent the avoidable emission of smoke, and failure to comply is an offence. It is evident that the contribution of motor vehicles to Air Pollution has been recognised in Britain, but the Final Report of the Beaver Committee (3) comments that the Committee were unable to find any evidence that the police, who are charged with enforcement of the law, have, in fact, ever apprehended offenders.

Of special interest are the powers given originally to Manchester and later extended to London and other cities to prescribe "smokeless zones"; i.e., designated areas within which it shall be a statutory offence to emit any kind of visible smoke (4). These zones are necessarily residential and/or commercial areas of cities, and by this means, private dwellings which contribute significant amounts of pollution are brought under control. No legislation of this type has yet been enacted in North America to our knowledge. At the present time, the British Parliament is considering a bill known as the Clean Air Bill to implement the recommendations of a Royal Commission (3) set up under the chairmanship of Sir Hugh Beaver following the disastrous fog of December, 1952 during which 4000 persons died in London. This bill requires local authorities to proceed as quickly as possible with the creation of smoke-reduction zones similar to the smokeless zone in concept but aiming at 80% reduction in smoke instead of 100% reduction. Industrial smoke is likewise under the control of the local authority and the Beaver Report recommends that "dark smoke", defined as Rengelmann No. 2 or greater, should be prohibited except for a period not exceeding six minutes in any four-hour period with waivers for lighting up or mechanical failure. There seems to be no reason why this smokeless zone idea should not be enforced in all new subdivisions in Canada, or in a large proportion of those built since world war II. Detailed consideration of the provisions of the Clean Air Bill is unnecessary since this bill is designed to deal with conditions having no counterpart in Canada and it is unlikely that similar legislation will ever be required. Of greater interest to Canadian Industry is the Alkali Trades Act which was first passed in Britain nearly 100 years ago when the effluent problem first began to threaten England's "green and pleasant land".

The salt-cake process for the production of caustic alkali evolved large quantities of unwanted gas, hydrochloric acid, which was vented to the atmosphere to the detriment of the surrounding property and persons. Up to that time, the procedure in the case of such a nuisance had been to prohibit it, but a Royal Commission set up to study

the complaints was farsighted enough to recognize that this might be the beginnings of a new chemical industry and recommended the installation of scrubbers to remove at least 95% of the acid gas. They also made a series of recommendations which were embodied in the first Alkali Act passed in 1863 and, after a trial period of five years, the Act was such a success that its scope was extended to cover a number of other industries.

The provisions of the Act were summarized very well by the Chief Inspector in a paper given at the U.S. technical Conference on Air Pollution held in New York in 1952 (5). The following excerpt is taken from this paper.

"The main principles are that:

1. No process described in the schedule shall operate without being registered.
2. A prior condition of registration shall be that the works is furnished with the "best practicable means" for preventing the escape of noxious or offensive gases or for rendering them harmless and inoffensive.
3. A list of noxious or offensive gases is given in the Act. This list has been extended from time to time:
4. A scheduled work is required to use the means mentioned in (2) above, continuously and to maintain it in good and efficient order.
5. "Best practicable means" is defined as having reference not only to the provision and efficient maintenance of appliances for preventing escapes of noxious or offensive gases but also to the manner in which such appliances are used and to the proper supervision by the owners of any operation in which such gases are evolved.
6. In certain cases rigid limits are laid down for the escape of acid gases, e.g.,

Alkali works. At least 95 per cent. condensation of the HCl evolved and the escape not to exceed 0.2 grain HCl per cu. ft.

Sulfuric acid (lead chamber) works. The undiluted escape not to exceed the equivalent of 4 grains SO_3 per cu. ft.

Sulfuric acid concentration works. The escape not to exceed the equivalent of 1.5 grains SO_3 per cu. ft.

Muriatic acid works. The escape not to exceed 0.2 grain HCl per cu. ft.

7. Registered works are subject to inspection to ensure compliance with the regulations.

8. Penalties are prescribed for infringement of the regulations.

Except for the four processes mentioned above no legal limits of concentration for escaping gases have been made, reliance being placed on the phrase "best practicable means". The chief inspector has therefore to decide what is the best practicable means in every case and in doing so, he should endeavor to reconcile the natural desire of local residents to enjoy an uncontaminated atmosphere with the legitimate aspirations of manufacturers."

Other industry co-operates with the Inspector voluntarily although under no compulsion to do so except the fear of a further extension of section (3) above.

Under this Act, with the exception of the four acid gases noted, no hard and fast limits are placed in the quality of any effluent, no time-consuming legal processes are needed to change the required standards in the light of technical advances and no manufacturer is penalized by local factors beyond his control which might make it impossible for him to reach the usual standards. Over the years, the inspector has developed a number of "presumptive standards" which have no legal force but are used solely as guides and can be amended whenever there is justification for doing so.

This, then, represents briefly the status of air pollution legislation in Britain today, but before discussing the merits of this type of legislation, I would like to consider not only what air pollution control legislation is trying to do but also what problems industrial management are having to face in order to comply with these laws. It must be conceded that industry must make some pollution and it must be recognised that unduly severe restrictions quickly bring the law into disrespect. Under totalitarian rule, restrictive laws can be made to work, but in a democracy a large degree of public support is essential if a law is to be effective. It is now becoming recognised in the matter of traffic speed restrictions that the 85 percentile speed represents the minimum speed which can be enforced successfully. By the same token, pollution control laws must command a considerable amount of support for success. It must also be conceded that industry is anxious to avoid litigation and will spend large sums of money to ensure freedom from law suits. Unfortunately, our present knowledge precludes the setting up of rigid effluent standards, compliance with which would confer immunity from litigation. It is, of course, grossly unfair to grant an injunction against a firm to cease to commit a nuisance without specifying what lower level of pollution would be considered satisfactory. Even the smallest amount of pollution might be held to be a violation of the injunction and the plant is in fact virtually prevented from operating. The British law overcomes this difficulty by making "nuisance" a statutory nuisance for which the "best possible means" of suppression is an adequate defence and then by creating an inspector to decide and enforce the best possible means. In this way, actions for nuisance are rare. While this may seem to bypass the courts of justice, I believe that the Alkali Inspector is more likely to make a fair decision (if not always the legally correct decision) than is a judge unskilled in the subtleties of scientific measurement and investigation, when confronted by "experts" of differing opinions who are not necessarily sufficiently skilled in the cross-examination technique of the courts to convey accurately to the layman the true interpretation of their scientific findings.

Scientists have been warned by members of the legal profession that "the most thorough scientist makes a much weaker impression on a judge and jury than the superficial 'expert' who states positively an opinion without the reservations caused by a more complete knowledge of the subject" (6) and that the Court of Law is not the place "where the cards are laid on the table in the naive hope that the 'right' conclusion

will be reached" (7). In an "open-forum" discussion, the thorough scientist would probably quickly demonstrate the effect of factors ignored by the superficial expert. Under the present judicial system, I fear many verdicts are dependent more on the personality of witnesses than reliability of opinion.

Apart from the purely local complaints of industrial pollution there is a growing problem of what may be termed chronic pollution as opposed to the acute type of pollution so prevalent in the past. By this, I mean the pollution problem typified at present by the Los Angeles Smog problem which is due to the accumulative effect of a large metropolis outgrowing the capacity of the local atmosphere to maintain a sufficient supply of fresh air. There are signs that this type of problem is going to arise much more frequently in the future. Undoubtedly, morbidity and mortality records tend to show that the smokiness of our city atmospheres has an effect on the health of the inhabitants. The wholesale change-over to oil and gas for heating, to diesel and gasoline engines for transport, appears to have substituted an invisible pollutant for the visible smoke. This build-up of pollution from innumerable minute sources is much more difficult to control than the acute problem presented by large chimneys, and constant watch and careful study will be needed to prevent the growth of a strong public opinion which has resulted elsewhere in political expediency over-riding technical caution and giving rise to hurried and ineffective legislation.

Without proper assessment of the causes of the smog, restrictive laws, patterned after the accepted smoke abatement laws, have been passed and rigorously enforced. These laws have done little to improve the smog condition while prejudicing co-operation by industry whose skill and knowledge are of the greatest value. From the purely technical point of view, it would be preferable to secure the co-operation of industry to make a careful technical study of the area prior to setting up legislation and our work at Sarnia shows that this can be done if a start is made sufficiently early before conditions have deteriorated to the point where the public demand immediate action.

Air pollution legislation is a very complex problem. It is made no easier by the fact that almost every air pollution problem is different and needs individual treatment. Legislation therefore needs to be flexible to meet the innumerable conditions existing throughout the country. This could be achieved by permissive legislation granting local authorities wide discretionary powers, but experience has shown that local authorities are not competent to exercise discretion, neither do they have the financial resources to attract the necessary skilled staff to handle their problems successfully. The record of Great Britain in the control of pollutants other than smoke and the absence of long and costly lawsuits during nearly 100 years of operation under the Alkali Trades Act suggests that this is one field where the expert knows best - and "do-it-yourself" kits are not to be recommended.

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